

Quantum Mechanics

Solutions to Graduate Exam

Summer, 2022

Each problem is worth 25 points. The points for individual parts are marked in square brackets. **To ensure full credit, show your work.** Do any four (4) of the following five (5) problems. If you attempt all 5 problems you must clearly state which 4 problems you want to have graded.

1. A particle of mass m is in the potential $V(x) = \begin{cases} \lambda \delta(x - \frac{1}{2}a) & 0 < x < a, \\ \infty & \text{otherwise,} \end{cases}$ where λ is small.

(a) [5] What are the exact eigenstate wave functions and energies of the states if $\lambda = 0$?

If $\lambda = 0$, this is just the infinite square well, with eigenstates and energies

$$\phi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right), \quad \varepsilon_n = \frac{\pi^2 \hbar^2 n^2}{2ma^2}, \quad n = 1, 2, 3, \dots$$

(b) [20] What is the ground state eigenstate to first order and its energy to second order in λ ? You may leave the eigenstate as an infinite sum, but for full credit you must perform any sums explicitly (possibly helpful formulas below)

The ground state to first order and the energy to second order are given by

$$|\psi_1\rangle = |\phi_1\rangle + \sum_{n \neq 1} |\phi_n\rangle \frac{\langle \phi_n | W | \phi_1 \rangle}{\varepsilon_1 - \varepsilon_n},$$

$$E_1 = \varepsilon_1 + \langle \phi_1 | W | \phi_1 \rangle + \sum_{n \neq 1} \frac{|\langle \phi_n | W | \phi_1 \rangle|^2}{\varepsilon_1 - \varepsilon_n}.$$

The matrix elements we need are

$$\langle \phi_n | W | \phi_1 \rangle = \lambda \int \phi_n^*(x) \delta(x - \frac{1}{2}a) \phi_1(x) dx = \lambda \frac{2}{a} \sin\left(\frac{\pi n a}{2a}\right) = \frac{2\lambda}{a} \sin\left(\frac{\pi n}{2}\right).$$

The last factor vanishes for any even n , and gives alternately +1 or -1 for $n = 1, 3, 5$, etc. The resulting eigenstate will be given by

$$|\psi_1\rangle = |\phi_1\rangle + \frac{2\lambda}{a} \sum_{n=1}^{\infty} (-1)^n |\phi_{2n+1}\rangle \frac{2ma^2}{\pi^2 \hbar^2 [1 - (2n+1)^2]} = |\phi_1\rangle + \frac{\lambda ma}{\pi^2 \hbar^2} \sum_{n=1}^{\infty} \frac{(-1)^{n-1}}{n^2 + n} |\phi_{2n+1}\rangle.$$

We still have to find the energy of the modified ground state, which is

$$E_1 = \frac{\pi^2 \hbar^2}{2ma^2} + \frac{2\lambda}{a} + \sum_{n \neq 1} \left(\frac{2\lambda}{a} \right)^2 \sin^2 \left(\frac{\pi n}{2} \right) \frac{2ma^2}{\pi^2 \hbar^2 (1-n^2)}$$

$$= \frac{\pi^2 \hbar^2}{2ma^2} + \frac{2\lambda}{a} - \frac{8m\lambda^2}{\pi^2 \hbar^2} \sum_{n=1}^{\infty} \frac{1}{(2n+1)^2 - 1} = \frac{\pi^2 \hbar^2}{2ma^2} + \frac{2\lambda}{a} - \frac{2m\lambda^2}{\pi^2 \hbar^2}.$$

Sum Formulas

$$\sum_{n=2}^{\infty} \frac{1}{n^2 - 1} = \frac{3}{4}, \quad \sum_{n=1}^{\infty} \frac{1}{(2n)^2 - 1} = \frac{1}{2}, \quad \sum_{n=1}^{\infty} \frac{1}{(2n+1)^2 - 1} = \frac{1}{4},$$

$$\sum_{n=2}^{\infty} \frac{(-1)^n}{n^2 - 1} = \frac{1}{4}, \quad \sum_{n=1}^{\infty} \frac{(-1)^n}{(2n)^2 - 1} = \frac{1}{2} - \frac{\pi}{4}, \quad \sum_{n=1}^{\infty} \frac{(-1)^n}{(2n+1)^2 - 1} = \frac{1}{4} - \frac{\ln(2)}{2},$$

2. The electron in a hydrogen atom is in the 3d orbital in the state

$$|l, s, m_l, m_s\rangle = |2, \frac{1}{2}, 1, -\frac{1}{2}\rangle.$$

- (a) [7] If you measure $\mathbf{J}^2 = (\mathbf{L} + \mathbf{S})^2$ in this state, what are the corresponding possible j -values and their corresponding probabilities? You may consult the Clebsch-Gordan coefficient values given below.

When you add angular momentum 2 to angular momentum $\frac{1}{2}$, the results range from $|l-s| = \frac{3}{2}$ to $l+s = \frac{5}{2}$, so the only possible results are $j = \frac{3}{2}, \frac{5}{2}$. If such a measurement were made, the state would go from an $|l, s, m_l, m_s\rangle$ state to one of the $|l, s, j, m_j\rangle$ eigenstates. The values of l and s will be unchanged, and the value of $m_j = m_l + m_s = 1 - \frac{1}{2} = \frac{1}{2}$ would be unchanged. The corresponding probabilities would be given by

$$P(j = \frac{3}{2}) = \left| \langle \frac{3}{2}, \frac{1}{2} | 2, \frac{1}{2}; 1, -\frac{1}{2} \rangle \right|^2 = \left| -\sqrt{\frac{3}{5}} \right|^2 = \frac{3}{5}, \quad \text{and} \quad P(j = \frac{5}{2}) = \left| \langle \frac{5}{2}, \frac{1}{2} | 2, \frac{1}{2}; 1, -\frac{1}{2} \rangle \right|^2 = \left| \sqrt{\frac{2}{5}} \right|^2 = \frac{2}{5}.$$

- (b) [6] For each outcome in part (a), compute the value of $\mathbf{L} \cdot \mathbf{S} = \frac{1}{2}(\mathbf{J}^2 - \mathbf{L}^2 - \mathbf{S}^2)$.

The value is simply

$$\mathbf{L} \cdot \mathbf{S} = \frac{1}{2}(\mathbf{J}^2 - \mathbf{L}^2 - \mathbf{S}^2) = \frac{1}{2}\hbar^2 (j^2 + j - l^2 - l - s^2 - s) = \frac{1}{2}\hbar^2 (j^2 + j - \frac{27}{4}) = \begin{cases} \hbar^2 & \text{for } j = \frac{5}{2}, \\ -\frac{3}{2}\hbar^2 & \text{for } j = \frac{3}{2}. \end{cases}$$

- (c) [6] Combining the above information, deduce the expectation value of $\mathbf{L} \cdot \mathbf{S}$ for the initial state given.

The expectation value is simply the result times the corresponding probability, so

$$\langle \mathbf{L} \cdot \mathbf{S} \rangle = \frac{3}{5} \left(-\frac{3}{2} \hbar^2 \right) + \frac{2}{5} \left(\hbar^2 \right) = -\frac{5}{10} \hbar^2 = -\frac{1}{2} \hbar^2.$$

(d) [6] Finally, show that $\mathbf{L} \cdot \mathbf{S} = \frac{1}{2} (L_+ S_- + L_- S_+) + L_z S_z$, where $L_{\pm} = L_x \pm iL_y$ and $S_{\pm} = S_x \pm iS_y$, and use this to check the result by computing $\langle 2, \frac{1}{2}, 1, -\frac{1}{2} | \mathbf{L} \cdot \mathbf{S} | 2, \frac{1}{2}, 1, -\frac{1}{2} \rangle$ in the original basis.

Simply substituting in the expressions, we have

$$\begin{aligned} \frac{1}{2} (L_+ S_- + L_- S_+) + L_z S_z &= \frac{1}{2} \left[(L_x + iL_y)(S_x - iS_y) + (L_x - iL_y)(S_x + iS_y) \right] + L_z S_z \\ &= \frac{1}{2} (2L_x S_x + 2L_y S_y) + L_z S_z = \mathbf{L} \cdot \mathbf{S}. \end{aligned}$$

Now, when we let this combination of operators act on the state, all the terms with L_{\pm} or S_{\pm} will change the values of m_l and m_s , which means it has no overlap with itself. The only remaining term is $L_z S_z$, and it is an eigenstate of these two operators with eigenvalues $\hbar m_l$ and $\hbar m_s$, so we have

$$\begin{aligned} \langle 2, \frac{1}{2}, 1, -\frac{1}{2} | \mathbf{L} \cdot \mathbf{S} | 2, \frac{1}{2}, 1, -\frac{1}{2} \rangle &= \langle 2, \frac{1}{2}, 1, -\frac{1}{2} | L_z S_z | 2, \frac{1}{2}, 1, -\frac{1}{2} \rangle = \langle 2, \frac{1}{2}, 1, -\frac{1}{2} | \hbar(1) \hbar(-\frac{1}{2}) | 2, \frac{1}{2}, 1, -\frac{1}{2} \rangle \\ &= -\frac{1}{2} \hbar^2. \end{aligned}$$

So it worked out as it should.

Raising and Lowering Angular Momentum: $J_{\pm} |j, m\rangle = \hbar \sqrt{j(j+1) - m(m \pm 1)} |j, m \pm 1\rangle$

Clebsch-Gordan Coefficients: $\langle j_1 j_2; m_1 m_2 | jm \rangle$ for $j_1, j_2 = 2, \frac{1}{2}$ and $m > 0$: $\langle 2 \frac{1}{2}; 2 \frac{1}{2} | \frac{5}{2} \frac{5}{2} \rangle = 1$

$$\begin{aligned} \langle 2 \frac{1}{2}; 1 \frac{1}{2} | \frac{5}{2} \frac{3}{2} \rangle &= \sqrt{\frac{4}{5}}, & \langle 2 \frac{1}{2}; 2 \frac{-1}{2} | \frac{5}{2} \frac{3}{2} \rangle &= \sqrt{\frac{1}{5}}, & \langle 2 \frac{1}{2}; 1 \frac{1}{2} | \frac{3}{2} \frac{3}{2} \rangle &= \sqrt{\frac{1}{5}}, & \langle 2 \frac{1}{2}; 2 \frac{-1}{2} | \frac{3}{2} \frac{3}{2} \rangle &= -\sqrt{\frac{4}{5}}, \\ \langle 2 \frac{1}{2}; 0 \frac{1}{2} | \frac{5}{2} \frac{1}{2} \rangle &= \sqrt{\frac{3}{5}}, & \langle 2 \frac{1}{2}; 1 \frac{-1}{2} | \frac{5}{2} \frac{1}{2} \rangle &= \sqrt{\frac{2}{5}}, & \langle 2 \frac{1}{2}; 0 \frac{1}{2} | \frac{3}{2} \frac{1}{2} \rangle &= \sqrt{\frac{2}{5}}, & \langle 2 \frac{1}{2}; 1 \frac{-1}{2} | \frac{3}{2} \frac{1}{2} \rangle &= -\sqrt{\frac{3}{5}}. \end{aligned}$$

3. Estimate the ground state energy of the hydrogen atom (potential $V = -\beta/r$), by the variational method using the trial wave function $\psi(r) = \begin{cases} a-r & \text{if } r < a, \\ 0 & \text{if } r > a, \end{cases}$ and compare the resulting value with the exact answer $E = -\beta^2 m / (2\hbar^2)$.

The trial wave function is obviously not normalized, so we have to incorporate the normalization factor into our computations. We will have to perform three integrations, all of which will be spherically symmetric. We therefore have

$$\begin{aligned}
\langle \psi | \psi \rangle &= \int \psi^*(\mathbf{r}) \psi(\mathbf{r}) d^3\mathbf{r} = 4\pi \int_0^\infty r^2 |\psi(r)|^2 dr = 4\pi \int_0^a r^2 (a-r)^2 dr \\
&= 4\pi \left(\frac{1}{5} r^5 - \frac{2}{4} a r^4 + \frac{1}{3} r^3 a \right) \Big|_0^a = \frac{2}{15} \pi a^5, \\
\langle \psi | \mathbf{P}^2 | \psi \rangle &= -\hbar^2 \int \psi^*(\mathbf{r}) \nabla^2 \psi(\mathbf{r}) d^3\mathbf{r} = -4\pi \hbar^2 \int_0^\infty r^2 \psi^*(r) \frac{1}{r} \frac{d^2}{dr^2} (r\psi) dr \\
&= -4\pi \hbar^2 \int_0^a r^2 (a-r) \frac{1}{r} \frac{d^2}{dr^2} (ar - r^2) dr \\
&= 8\pi \hbar^2 \int_0^a (ar - r^2) dr = 8\pi \hbar^2 \left(\frac{1}{2} ar^2 - \frac{1}{3} r^3 \right) \Big|_0^a = \frac{4}{3} \pi \hbar^2 a^3, \\
\langle \psi | V | \psi \rangle &= \int \psi^*(\mathbf{r}) \psi(\mathbf{r}) V(\mathbf{r}) d^3\mathbf{r} = -4\pi \beta \int_0^\infty r |\psi(r)|^2 dr = -4\pi \beta \int_0^a r (a-r)^2 dr \\
&= -4\pi \beta \left(\frac{1}{2} a^2 r^2 - \frac{2}{3} ar^3 + \frac{1}{4} r^4 \right) \Big|_0^a = -\frac{1}{3} \pi \beta a^4.
\end{aligned}$$

We now use this to get the normalized expectation value of the Hamiltonian, which is given by

$$E(a) = \frac{1}{\langle \psi | \psi \rangle} \left(\frac{1}{2m} \langle \psi | \mathbf{P}^2 | \psi \rangle + \langle \psi | V | \psi \rangle \right) = \frac{15}{2\pi a^5} \left(\frac{2\pi \hbar^2 a^3}{3m} - \frac{\pi \beta a^4}{3} \right) = \frac{5\hbar^2}{ma^2} - \frac{5\beta}{2a}.$$

To find an estimate of the energy, we find the minimum of this function, which is when the derivative vanishes, so we have

$$\begin{aligned}
0 &= \frac{d}{da} E(a) = -\frac{10\hbar^2}{ma^3} + \frac{5\beta}{2a^2}, \\
20\hbar^2 a^2 &= 5\beta m a^3, \\
a_0 &= \frac{4\hbar^2}{\beta m}.
\end{aligned}$$

Substituting this back into the formula for the energy, we have

$$E(a_0) = \frac{5\hbar^2}{m} \left(\frac{\beta m}{4\hbar^2} \right)^2 - \frac{5\beta}{2} \left(\frac{\beta m}{4\hbar^2} \right) = \frac{\beta^2 m}{\hbar^2} \left(\frac{5}{16} - \frac{5}{8} \right) = -\frac{5\beta^2 m}{16\hbar^2}.$$

This is identical with the exact formula except that the factor of 5/16 in this should be 1/2, which means our energy is too high (as it always must be from the variational principle).

Possibly Useful Formula $\nabla^2 \psi = \frac{1}{r} \frac{\partial^2}{\partial r^2} (r\psi) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2}$

4. Imagine a system in which there are just two linearly independent states $\{|1\rangle, |2\rangle\}$, and the Hamiltonian, represented as a matrix in this basis, is $\hat{H} = \begin{pmatrix} h & g \\ g & h \end{pmatrix}$, where g and h are real constants.

(a) [9] Find the eigenvalues and (normalized) eigenvectors of this Hamiltonian.

The Hamiltonian is $\hat{H} = h\mathbf{1} + g\sigma_x$, where $\mathbf{1}$ is the identity matrix and σ_x is the Pauli matrix. All vectors are eigenvectors of $\mathbf{1}$, so this means we simply have to diagonalize σ_x . But the eigenstates of σ_x are well known, and are simply

$$|\phi_+\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix} \quad \text{and} \quad |\phi_-\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix},$$

with eigenvalues ± 1 under σ_x . Incorporating the factor of g and including the effects of $h\mathbf{1}$, these are still eigenvectors but with eigenvalues $E_{\pm} = h \pm g$. For future reference we will notice that $\frac{1}{\sqrt{2}}(|\phi_+\rangle + |\phi_-\rangle) = |1\rangle$ and $\frac{1}{\sqrt{2}}(|\phi_+\rangle - |\phi_-\rangle) = |2\rangle$.

(b) [9] Suppose the system starts out at $t = 0$ in state $|1\rangle$. What is the state at time t ?

We start in the state $|\Psi(0)\rangle = |1\rangle = \frac{1}{\sqrt{2}}(|\phi_+\rangle + |\phi_-\rangle)$. Each of the eigenstates now just picks up a factor of $e^{-iE_{\pm}t/\hbar}$, so we have

$$\begin{aligned} |\Psi(t)\rangle &= \frac{1}{\sqrt{2}}(|\phi_+\rangle e^{-iE_+t/\hbar} + |\phi_-\rangle e^{-iE_-t/\hbar}) = \frac{1}{\sqrt{2}} e^{-iht/\hbar} (|\phi_+\rangle e^{-igt/\hbar} + |\phi_-\rangle e^{igt/\hbar}) \\ &= \frac{1}{\sqrt{2}} e^{-iht/\hbar} \{ |\phi_+\rangle [\cos(gt/\hbar) - i \sin(gt/\hbar)] + |\phi_-\rangle [\cos(gt/\hbar) + i \sin(gt/\hbar)] \} \\ &= e^{-iht/\hbar} \left[\cos(gt/\hbar) \frac{1}{\sqrt{2}}(|\phi_+\rangle + |\phi_-\rangle) + i \sin(gt/\hbar) \frac{1}{\sqrt{2}}(-|\phi_+\rangle + |\phi_-\rangle) \right] \\ &= e^{-iht/\hbar} [\cos(gt/\hbar)|1\rangle - i \sin(gt/\hbar)|2\rangle]. \end{aligned}$$

(c) [7] What is the probability that it will still be in state $|1\rangle$ at time $t = \pi\hbar/2g$?

The probability at arbitrary time is

$$P(1) = \left| \langle 1 | \Psi(t) \rangle \right|^2 = \left| e^{-iht/\hbar} \cos(gt/\hbar) \right|^2 = \cos^2\left(\frac{gt}{\hbar}\right).$$

In particular, the probability at $t = \pi\hbar/2g$ is $\cos^2(\frac{1}{2}\pi) = 0$.

5. An electron is in the spin state $|\chi\rangle = A \begin{pmatrix} 3i \\ 4 \end{pmatrix}$ in the standard basis of eigenstates of S_z .

(a) [4] Determine the normalization constant A .

To be normalized, we must have

$$1 = \langle \chi | \chi \rangle = A^* \begin{pmatrix} -3i & 4 \end{pmatrix} A \begin{pmatrix} 3i \\ 4 \end{pmatrix} = A^* A (-9i^2 + 16) = 25 A^* A.$$

Up to an irrelevant phase factor, therefore, we must have $A = \frac{1}{5}$.

(b) [8] Find the expectation value of S_x , S_y , and S_z .

We simply calculate each of these in turn.

$$\langle S_x \rangle = \langle \chi | S_x | \chi \rangle = \frac{1}{2} \cdot \frac{1}{25} \hbar \begin{pmatrix} -3i & 4 \end{pmatrix} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 3i \\ 4 \end{pmatrix} = \frac{1}{50} \hbar \begin{pmatrix} -3i & 4 \end{pmatrix} \begin{pmatrix} 4 \\ 3i \end{pmatrix} = 0,$$

$$\langle S_y \rangle = \langle \chi | S_y | \chi \rangle = \frac{1}{2} \cdot \frac{1}{25} \hbar \begin{pmatrix} -3i & 4 \end{pmatrix} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \begin{pmatrix} 3i \\ 4 \end{pmatrix} = \frac{1}{50} \hbar \begin{pmatrix} -3i & 4 \end{pmatrix} \begin{pmatrix} -4i \\ -3 \end{pmatrix} = -\frac{24}{50} \hbar,$$

$$\langle S_z \rangle = \langle \chi | S_z | \chi \rangle = \frac{1}{2} \cdot \frac{1}{25} \hbar \begin{pmatrix} -3i & 4 \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} 3i \\ 4 \end{pmatrix} = \frac{1}{50} \hbar \begin{pmatrix} -3i & 4 \end{pmatrix} \begin{pmatrix} 3i \\ -4 \end{pmatrix} = -\frac{7}{50} \hbar.$$

(c) [7] Find the uncertainties for these measurements.

The first thing we need to calculate is $\langle S_i^2 \rangle$ for each of the three operators. But

$S_i^2 = \left(\frac{1}{2} \hbar \sigma_i\right)^2 = \frac{1}{4} \hbar^2 \sigma_i^2 = \frac{1}{4} \hbar^2$, so independent of the state we know that

$$\langle S_x^2 \rangle = \langle S_y^2 \rangle = \langle S_z^2 \rangle = \frac{1}{4} \hbar^2.$$

We now substitute each of these into the definition of the uncertainty to yield

$$\Delta S_x = \sqrt{\langle S_x^2 \rangle - \langle S_x \rangle^2} = \sqrt{\frac{1}{4} \hbar^2 - (0)^2} = \frac{1}{2} \hbar,$$

$$\Delta S_y = \sqrt{\langle S_y^2 \rangle - \langle S_y \rangle^2} = \sqrt{\frac{1}{4} \hbar^2 - \left(-\frac{24}{50} \hbar\right)^2} = \frac{7}{50} \hbar,$$

$$\Delta S_z = \sqrt{\langle S_z^2 \rangle - \langle S_z \rangle^2} = \sqrt{\frac{1}{4} \hbar^2 - \left(-\frac{7}{50} \hbar\right)^2} = \frac{24}{50} \hbar = \frac{12}{25} \hbar.$$

(d) [6] Confirm your results are consistent with all three generalized uncertainty relations for these observables.

The generalized uncertainty relation tells us that if A and B are two operators, then $\Delta A \Delta B \geq \frac{1}{2} |\langle [A, B] \rangle|$. Working them in pairs, this implies $\Delta S_x \Delta S_y \geq \frac{1}{2} \hbar |\langle S_z \rangle|$, $\Delta S_y \Delta S_z \geq \frac{1}{2} \hbar |\langle S_x \rangle|$, and $\Delta S_z \Delta S_x \geq \frac{1}{2} \hbar |\langle S_y \rangle|$. Substituting our explicit values, we find

$$\Delta S_x \Delta S_y = \left(\frac{1}{2} \hbar\right) \left(\frac{7}{50} \hbar\right) = \frac{7}{100} \hbar^2 \geq \frac{1}{2} \hbar \frac{7}{50} \hbar = \frac{7}{100} \hbar^2,$$

$$\Delta S_y \Delta S_z = \left(\frac{7}{50} \hbar\right) \left(\frac{12}{25} \hbar\right) = \frac{42}{625} \hbar^2 \geq \frac{1}{2} \hbar 0 = 0,$$

$$\Delta S_z \Delta S_x = \left(\frac{12}{25} \hbar\right) \left(\frac{1}{2} \hbar\right) = \frac{6}{25} \hbar^2 \geq \frac{1}{2} \hbar \frac{12}{25} \hbar = \frac{6}{25} \hbar^2.$$

Obviously, the first and last are equalities and the middle one is true as well.

Possibly Helpful Formulas:

$$S_i = \frac{1}{2} \hbar \sigma_i, \quad \sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \quad \sigma_i^2 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}.$$