Quantum Mechanics
Solutions to Graduate Exam

Summer, 2023

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. Some possibly helpful formulas are given at the end of the exam.

1. Consider a particle of mass *m* in a two-dimensional infinite square well with allowed region $0 < x < a$ and $0 < y < a$. In addition, there is a small perturbation with potential

$$W(x,y) = \begin{cases} w_0 & \text{if } 0 < x < \tfrac{1}{2}a, 0 < y < \tfrac{1}{2}a, \\ 0 & \text{otherwise.} \end{cases}$$

(a)[5] What are the unperturbed energy eigenvalues and corresponding wave functions?

The unperturbed states of the 1D infinite square well are $\psi_n(x) = \sqrt{2/a}\sin(\pi n x/a)$ with energy $\varepsilon_n = \pi^2\hbar^2 n^2 / 2ma^2$. In 2D, we multiply these wave functions and add their energies, so the wave functions and energies are

$$\psi_{n_x n_y}(x,y) = \frac{2}{a}\sin\left(\frac{\pi n_x x}{a}\right)\sin\left(\frac{\pi n_y y}{a}\right), \quad \varepsilon_{n_x n_y} = \frac{\pi^2\hbar^2}{2ma^2}\left(n_x^2 + n_y^2\right).$$

The ground state is $|\psi_{11}\rangle$, but the first excited states are degenerate, $|\psi_{12}\rangle$ and $|\psi_{21}\rangle$.

(b) [8] Calculate, to first order in w_0, the perturbed energy of the ground state.

The leading correction to the energy is $\langle\psi_{11}|W|\psi_{11}\rangle$, which works out to

$$\varepsilon'_{11} = \langle\psi_{11}|W|\psi_{11}\rangle = w_0\int_0^{a/2} dx \int_0^{a/2} |\psi_{11}|^2\, dy = w_0\left(\frac{2}{a}\right)^2 \int_0^{a/2}\sin^2\left(\frac{\pi x}{a}\right)dx \int_0^{a/2}\sin^2\left(\frac{\pi y}{a}\right)dy$$

$$= w_0\frac{4}{a^2}\left(\frac{a}{4}\right)^2 = \frac{1}{4}w_0.$$

Adding this to the unperturbed energy, the total energy is approximately

$$E_{11} = \varepsilon_{11} + \varepsilon'_{11} = \frac{\pi^2\hbar^2}{ma^2} + \frac{1}{4}w_0.$$

(c) [12] Same question for the first excited state(s). Give the corresponding wave function(s) to zeroth order in w_0.

This time we are dealing with states that are degenerate, so we have to use degenerate perturbation theory. This requires that we work out the $\tilde{W}$ matrix, which is given by

$$\tilde{W} = \begin{pmatrix} \langle \psi_{21} | W | \psi_{21} \rangle & \langle \psi_{21} | W | \psi_{12} \rangle \\ \langle \psi_{12} | W | \psi_{21} \rangle & \langle \psi_{12} | W | \psi_{12} \rangle \end{pmatrix}.$$

The two off-diagonal pieces are complex conjugates of each other, so we need only work out one of them. The two on-diagonal ones end up looking very similar. We have

$$\langle \psi_{np} | W | \psi_{np} \rangle = w_0 \int_0^{a/2} dx \int_0^{a/2} |\psi_{21}|^2 \, dy = \frac{4w_0}{a^2} \int_0^{a/2} \sin^2\left(\frac{\pi n x}{a}\right) dx \int_0^{a/2} \sin^2\left(\frac{\pi p y}{a}\right) dy = \frac{4w_0}{a^2}\left(\frac{a}{4}\right)^2$$
$$= \frac{1}{4} w_0 ,$$

$$\langle \psi_{21} | W | \psi_{12} \rangle = w_0 \int_0^{a/2} dx \int_0^{a/2} \psi_{21}^* \psi_{12} dy$$
$$= \frac{4w_0}{a^2} \int_0^{a/2} \sin\left(\frac{2\pi x}{a}\right) \sin\left(\frac{\pi x}{a}\right) dx \int_0^{a/2} \sin\left(\frac{\pi y}{a}\right) \sin\left(\frac{2\pi y}{a}\right) dy$$
$$= \frac{4w_0}{a^2}\left(\frac{2a}{3\pi}\right)^2 = \frac{16}{9\pi^2} w_0 = \langle \psi_{12} | W | \psi_{21} \rangle .$$

Putting this all together, we have

$$\tilde{W} = w_0 \begin{pmatrix} \frac{1}{4} & \frac{16}{9\pi^2} \\ \frac{16}{9\pi^2} & \frac{1}{4} \end{pmatrix} = \frac{1}{4} w_0 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \frac{16}{9\pi^2} w_0 \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}.$$

The first term is proportional to the identity matrix, and every vector is an eigenvector of the identity matrix. The second one is proportional to σ_x, which has eigenvalues ± 1 and eigenvectors $|\psi_\pm\rangle = \frac{1}{\sqrt{2}}\left(|\psi_{21}\rangle \pm |\psi_{12}\rangle\right)$. Multiplying the eigenvalues by the factor out front and adding the constant term and also the unperturbed energy, the energy eigenvalues are given by

$$E_\pm = \frac{5\pi^2\hbar^2}{2ma^2} + \frac{1}{4} w_0 \pm \frac{16}{9\pi^2} w_0 ,$$

and the corresponding eigenstate wave functions will be

$$\psi_\pm(x, y) = \frac{\sqrt{2}}{a}\left[\sin\left(\frac{2\pi x}{a}\right)\sin\left(\frac{\pi y}{a}\right) \pm \sin\left(\frac{\pi x}{a}\right)\sin\left(\frac{2\pi y}{a}\right)\right].$$

2. A particle of mass *m* lies in a 1-D infinite square well with allowed region $0 < x < a$. At *t* = 0, the wave function is given by

$$\Psi(x,t=0)=\begin{cases}\sqrt{2/a} & \text{for } 0<x<\tfrac{1}{2}a, \\ 0 & \text{for } \tfrac{1}{2}a<x<a.\end{cases}$$

(a) [3] Will the particle remain localized in the left half of the well at later times?

Since the wave function is not an eigenstate of the Hamiltonian, it will not be an eigenstate, and it would be very surprising if it stayed in the initial region. In particular, it is possible to prove at $t = 2\pi ma^2/\hbar$ it will have moved entirely to the right half of the well, but we will not do so now.

(b) [7] The energy of the particle is measured. What is the probability that the result is the ground state energy E_1? What is the probability that the result is the first excited state energy E_2?

(c) [7] Calculate the probability that the energy yields the *n*'th state E_n.

In order to calculate these probabilities, we need to know the normalized eigenstates. These are simply given by

$$\phi_n(x)=\sqrt{\frac{2}{a}}\sin\left(\frac{\pi nx}{a}\right), \quad \text{with energy} \quad E_n=\frac{\pi^2\hbar^2n^2}{2ma^2}.$$

The probability that it is in a particular state is just the square of magnitude of the overlap with that state, so we have

$$P(n)=\left|\langle\phi_n|\Psi\rangle\right|^2=\left|\frac{2}{a}\int_0^{a/2}\sin\left(\frac{\pi nx}{a}\right)dx\right|^2=\left|-\frac{2}{a}\frac{a}{\pi n}\cos\left(\frac{\pi nx}{a}\right)\Big|_0^{a/2}\right|^2=\left\{\frac{2}{\pi n}\left[1-\cos\left(\frac{\pi n}{2}\right)\right]\right\}^2$$

$$=\frac{4}{\pi^2n^2}\left[1-\cos\left(\tfrac{1}{2}n\pi\right)\right]^2.$$

This is the general formula for part (c). In particular, this gives us for the first two cases

$$P(1)=\frac{4}{\pi^2}\left[1-\cos\left(\tfrac{1}{2}\pi\right)\right]^2=\frac{4}{\pi^2} \quad \text{and} \quad P(2)=\frac{1}{\pi^2}\left[1-\cos(\pi)\right]^2=\frac{4}{\pi^2}.$$

(d)[8] Show that the sum of the probabilities you found in part (c) is 1. The formula below may be useful.

$$\sum_{\substack{n=1\\ \text{odd}}}^{\infty}\frac{1}{n^2}=\frac{\pi^2}{8}$$

We need to think about $\cos\left(\frac{1}{2}n\pi\right)$ carefully. This takes successive values of 0, -1, 0, and 1, and then starts the cycle over again. Hence the expression $\left[1-\cos\left(\frac{1}{2}n\pi\right)\right]^2$ cycles through the values 1, 4, 1, 0. Hence the sum of probabilities is

$$\sum_{n=1}^{\infty} P(n) = \frac{4}{\pi^2}\left\{\frac{1}{1^2}+\frac{4}{2^2}+\frac{1}{3^2}+\frac{0}{4^2}+\frac{1}{5^2}+\frac{4}{6^2}+\frac{1}{7^2}+\frac{0}{8^2}+\cdots\right\}.$$

Discard the vanishing terms, and segregate the remainder into even and odd terms. We have

$$\sum_{n=1}^{\infty} P(n) = \frac{4}{\pi^2}\left\{\left(\frac{1}{1^2}+\frac{1}{3^2}+\frac{1}{5^2}+\frac{1}{7^2}+\cdots\right)+\left(\frac{4}{2^2}+\frac{4}{6^2}+\frac{4}{10^2}+\frac{4}{14^2}\cdots\right)\right\}.$$

Now, for all the even terms, cancel out the factors of two between numerator and denominator to yield

$$\sum_{n=1}^{\infty} P(n) = \frac{4}{\pi^2}\left\{\left(\frac{1}{1^2}+\frac{1}{3^2}+\frac{1}{5^2}+\frac{1}{7^2}+\cdots\right)+\left(\frac{1}{1^2}+\frac{1}{3^2}+\frac{1}{5^2}+\frac{1}{7^2}+\cdots\right)\right\} = \frac{4}{\pi^2}\cdot 2\sum_{\substack{n=1\\ \text{odd}}}^{\infty}\frac{1}{n^2} = \frac{8}{\pi^2}\cdot\frac{\pi^2}{8} = 1.$$

3. An electron of mass *m* is bound to a proton at the origin due to a potential $V(r) = -B/r$. Estimate the ground-state energy of this potential using the variational principle with trial wave function $\psi(r) = \begin{cases} a-r & \text{if } r<a, \\ 0 & \text{if } r>a, \end{cases}$ and compare to the exact energy $E_g = -\dfrac{mB^2}{2\hbar^2}$.

We will need to compute three quantities, namely

$$\langle\psi|\psi\rangle = \int |\psi(r)|^2 d^3\mathbf{r} = 4\pi\int_0^a (a-r)^2 r^2 dr = 4\pi\int_0^a \left(a^2r^2 - 2ar^3 + r^4\right)dr = 4\pi\left(\frac{a^5}{3}-\frac{a^5}{2}+\frac{a^5}{5}\right)$$
$$= \frac{2}{15}\pi a^5,$$

$$\left\langle \mathbf{P}^2\right\rangle = \left\|\mathbf{P}|\psi\rangle\right\|^2 = \int\left|-i\hbar\nabla\psi\right|^2 d^3\mathbf{r} = 4\pi\hbar^2\int_0^a \left|-\hat{\mathbf{r}}\right|^2 r^2 dr = \frac{4}{3}\pi\hbar^2 a^3,$$

$$\left\langle V(r)\right\rangle = -\int|\psi(r)|^2\frac{B}{r}d^3\mathbf{r} = -4\pi B\int_0^a (a-r)^2 r\,dr = -4\pi B\int_0^a\left(a^2r - 2ar^2 + r^3\right)dr$$
$$= -4\pi B\left(\frac{a^4}{2}-\frac{2a^4}{3}+\frac{a^4}{4}\right) = -\frac{1}{3}\pi B a^4.$$

We then need to calculate the energy expectation value, which is given by

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

In the variational approach, we minimize this with respect to a. The minimum occurs when

$$0 = \frac{d}{da}E(a) = -\frac{10\hbar^2}{ma^3} + \frac{5B}{2a^2},$$
$$20\hbar^2 a^2 = 5Bma^3,$$
$$a_{\min} = \frac{4\hbar^2}{mB}.$$

We then substitute this into the formula $E(a)$ to get our best estimate of the ground state energy:

$$E_g \approx E(a_{\min}) = \frac{5\hbar^2}{m}\left(\frac{mB}{4\hbar^2}\right)^2 - \frac{5B}{2}\left(\frac{mB}{4\hbar^2}\right) = \frac{mB^2}{\hbar^2}\left(\frac{5}{16} - \frac{5}{8}\right) = -\frac{5mB^2}{16\hbar^2}.$$

The exact energy is the same expression with $\frac{5}{16}$ replaced by $\frac{1}{2}$, which is lower, as it must be.

4. A single particle of mass *m* is in the 2D anisotropic harmonic oscillator with potential $V(x,y) = \frac{1}{2}m\omega^2 x^2 + \frac{1}{2}m(2\omega)^2 y^2$.

(a) [5] What are the energies of the states $\left|n_x, n_y\right\rangle$?

Both the x and y-directions are standard harmonic oscillators, except that in the y-direction the angular frequency is 2ω instead of ω. We simply add the energy in the two directions, making the appropriate substitutions, so

$$E_{n_x,n_y} = \hbar\omega_x\left(n_x + \tfrac{1}{2}\right) + \hbar\omega_y\left(n_y + \tfrac{1}{2}\right) = \hbar\omega\left(n_x + \tfrac{1}{2}\right) + 2\hbar\omega\left(n_y + \tfrac{1}{2}\right) = \hbar\omega\left(n_x + 2n_y + \tfrac{3}{2}\right).$$

(b)[8] At *t* = 0, the system is in the state $\left|\Psi(t=0)\right\rangle = \frac{1}{\sqrt{3}}\left(\left|1,0\right\rangle + \sqrt{2}\left|0,1\right\rangle\right)$. What is $\left|\Psi(t)\right\rangle$?

Since both of the states that comprise the starting state vector are energy eigenstates, we simply multiply them by $e^{-iEt/\hbar} = \exp\left[-i\omega\left(n_x + 2n_y + \tfrac{3}{2}\right)t\right]$. We therefore have

$$\left|\Psi(t)\right\rangle = \tfrac{1}{\sqrt{3}}\left(\left|1,0\right\rangle e^{-5i\omega t/2} + \sqrt{2}\left|0,1\right\rangle e^{-7i\omega t/2}\right).$$

(c) [12] What is the expectation value of $\left\langle XY\right\rangle$ for the state $\left|\Psi(t)\right\rangle$ from part (b) at all times *t*?

We rewrite our operators in terms of raising and lowering operators; however, in the y-direction, we have to replace ω by 2ω to take into account the higher frequency, so we have

$$XY = \sqrt{\frac{\hbar}{2m\omega_x}}\left(a_x + a_x^\dagger\right)\sqrt{\frac{\hbar}{2m\omega_y}}\left(a_y + a_y^\dagger\right) = \frac{\hbar}{2\sqrt{2}m\omega}\left(a_x + a_x^\dagger\right)\left(a_y + a_y^\dagger\right).$$

Letting this operate on the state $\left|\Psi(t)\right\rangle$ yields

$$XY\left|\Psi(t)\right\rangle = \frac{\hbar}{2\sqrt{6}m\omega}\left(a_x + a_x^\dagger\right)\left(a_y + a_y^\dagger\right)\left(\left|1,0\right\rangle e^{-5i\omega t/2} + \sqrt{2}\left|0,1\right\rangle e^{-7i\omega t/2}\right)$$
$$= \frac{\hbar}{2\sqrt{6}m\omega}\left(a_x + a_x^\dagger\right)\left(\left|1,1\right\rangle e^{-5i\omega t/2} + \sqrt{2}\left|0,0\right\rangle e^{-7i\omega t/2} + 2\left|0,2\right\rangle e^{-7i\omega t/2}\right)$$
$$= \frac{\hbar}{2\sqrt{6}m\omega}\left(\left|0,1\right\rangle e^{-5i\omega t/2} + \sqrt{2}\left|2,1\right\rangle e^{-5i\omega t/2} + \sqrt{2}\left|1,0\right\rangle e^{-7i\omega t/2} + 2\left|1,2\right\rangle e^{-7i\omega t/2}\right).$$

The requested expectation value is therefore

$$\left\langle\psi(t)\right|XY\left|\Psi(t)\right\rangle = \frac{\hbar}{2\sqrt{3}\sqrt{6}m\omega}\left(\left\langle 1,0\right| e^{5i\omega t/2} + \sqrt{2}\left\langle 0,1\right| e^{7i\omega t/2}\right)$$
$$\left(\left|0,1\right\rangle e^{-5i\omega t/2} + \sqrt{2}\left|2,1\right\rangle e^{-5i\omega t/2} + \sqrt{2}\left|1,0\right\rangle e^{-7i\omega t/2} + 2\left|1,2\right\rangle e^{-7i\omega t/2}\right)$$
$$= \frac{\hbar}{6\sqrt{2}m\omega}\left(\sqrt{2}e^{-i\omega t} + \sqrt{2}e^{i\omega t}\right) = \frac{2\sqrt{2}\hbar}{6\sqrt{2}m\omega}\cos(\omega t) = \frac{\hbar}{3m\omega}\cos(\omega t).$$

The result is real, as it must be.

5. A particle of mass *m* in the one-dimensional potential $V(x) = -B\delta(x)$ has only one bound state, with normalized wave function $\psi(x) = \sqrt{\lambda}e^{-\lambda|x|}$, with $\lambda\hbar^2 = Bm$. A particle is initially in this state at *t* = 0, but then the potential is shifted to a new position, so now $V(x) = -B\delta(x-a)$. What is the probability it remains bound if the shift is
(a) [8] gradual, or
(b) [17] sudden.

The bound state is obviously the ground state. After the delta-function has moved, the bound state wave function will be the same, but shifted to a new position. So our initial and final wave functions are $\psi_I(x) = \sqrt{\lambda}e^{-\lambda|x|}$ and $\psi_F(x) = \sqrt{\lambda}e^{-\lambda|x-a|}$.

If the motion is gradual, we use the adiabatic approximation, for which $P(I \to F) = 1$.

In contrast, if the move is sudden, we use the sudden approximation, which says that $P(I \to F) = \left|\left\langle\psi_F \middle| \psi_I\right\rangle\right|^2$. We now need to compute $\left\langle\psi_F \middle| \psi_I\right\rangle$, which we will do by splitting up the integral into three regions, so we have

$$\langle\psi_F|\psi_I\rangle = \int_{-\infty}^{\infty}\psi_F^*(x)\psi_I(x)\,dx = \lambda\int_{-\infty}^{\infty}\exp\left(-\lambda|x|-\lambda|x-a|\right)dx$$
$$= \lambda\int_{-\infty}^{0}\exp\left[\lambda x+\lambda(x-a)\right]dx + \lambda\int_0^a\exp\left[-\lambda x+\lambda(x-a)\right]dx$$
$$+\lambda\int_a^{\infty}\exp\left[-\lambda x-\lambda(x-a)\right]dx$$
$$= \lambda e^{-\lambda a}\int_{-\infty}^{0}e^{2\lambda x}dx + \lambda e^{-\lambda a}\int_0^a dx + \lambda e^{\lambda a}\int_a^{\infty}e^{-2\lambda x}dx$$
$$= \frac{\lambda}{2\lambda}e^{-\lambda a}\,e^{2\lambda x}\Big|_{-\infty}^{0} + a\lambda e^{-\lambda a} - \frac{\lambda}{2\lambda}e^{\lambda a}\,e^{-2\lambda x}\Big|_a^{\infty} = \frac{1}{2}e^{-\lambda a} + a\lambda e^{-\lambda a} + \frac{1}{2}e^{\lambda a}e^{-2\lambda a} = (1+\lambda a)e^{-\lambda a}.$$

Squaring this, we have the probability. In summary, our probabilities are

$$\text{adiabatic:}\quad P(I\to F)=1,$$
$$\text{sudden:}\quad P(I\to F)=(1+\lambda a)^2\,e^{-2\lambda a}.$$

Of course, we can rewrite our answers in terms of *B*, but this does nothing to simplify or clarify the results.

1D Harmonic Oscillator

Potential $\frac{1}{2}m\omega^2x^2$

$$X=\sqrt{\frac{\hbar}{2m\omega}}\left(a+a^\dagger\right),\quad a|n\rangle=\sqrt{n}\,|n-1\rangle,\quad a^\dagger|n\rangle=\sqrt{n+1}\,|n+1\rangle.$$

Operators in Spherical Coordinates

$$\nabla\psi=\hat{\mathbf{r}}\frac{\partial\psi}{\partial r}+\frac{1}{r}\hat{\boldsymbol{\theta}}\frac{\partial\psi}{\partial\theta}+\frac{1}{r\sin\theta}\hat{\phi}\frac{\partial\psi}{\partial\phi}$$
$$\nabla^2\psi=\frac{1}{r}\frac{\partial^2}{\partial r^2}(r\psi)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}$$

Possibly Helpful Integrals: In all formulas below, *n* and *p* are assumed to be positive integers.

$$\int\sin(\alpha x)\,dx=-\alpha^{-1}\cos(\alpha x),\quad \int\cos(\alpha x)\,dx=\alpha^{-1}\sin(\alpha x),\quad \int e^{\alpha x}dx=\alpha^{-1}e^{\alpha x}.$$
$$\int_0^{\infty}x^ne^{-Ax^2}dx=\tfrac{1}{2}A^{-(n+1)/2}\Gamma\left(\tfrac{n+1}{2}\right),\quad \int_0^{\infty}x^ne^{-Ax}dx=A^{-(n+1)}\Gamma(n+1),$$
$$\Gamma\left(\tfrac{1}{2}\right)=\sqrt{\pi},\quad \Gamma(1)=1,\quad \Gamma\left(\tfrac{3}{2}\right)=\tfrac{1}{2}\sqrt{\pi},\quad \Gamma(2)=1,\quad \Gamma\left(\tfrac{5}{2}\right)=\tfrac{3}{4}\sqrt{\pi},\quad \Gamma(3)=2.$$
$$\int_0^a\sin\left(\frac{\pi nx}{a}\right)\sin\left(\frac{\pi px}{a}\right)dx=\int_0^a\cos\left(\frac{\pi nx}{a}\right)\cos\left(\frac{\pi px}{a}\right)dx=\frac{a}{2}\delta_{np},$$
$$\int_0^a\sin\left(\frac{\pi nx}{a}\right)\cos\left(\frac{\pi px}{a}\right)dx=\frac{an}{\pi\left(n^2-p^2\right)}\left[1-(-1)^{n+p}\right].$$
$$\int_0^{a/2}\sin^2\left(\frac{\pi nx}{a}\right)dx=\int_0^{a/2}\cos^2\left(\frac{\pi nx}{a}\right)dx=\frac{a}{4},\quad \int_0^{a/2}\sin\left(\frac{\pi x}{a}\right)\sin\left(\frac{2\pi x}{a}\right)dx=\frac{2a}{3\pi}.$$