

Quantum Mechanics: SERP-CHEM
Final written test: 11/1/2013

Problem 1

A 1-dimensional harmonic oscillator with frequency ω is, at the time $t = 0$, in the state

$$\psi_0 = \frac{1}{\sqrt{2}} |0\rangle + \frac{1}{\sqrt{2}} |1\rangle + \frac{1}{\sqrt{5}} |3\rangle \quad (1)$$

where $|n\rangle$, with $n = 0, 1, 2, \dots$ are the normalized energy eigenstates with eigenvalues $E_n = \hbar\omega (n + \frac{1}{2})$.

- a) What is the average value of the energy at the time $t > 0$? (Points 5%)
- b) What is the average value of \hat{x}^2 on this state at $t > 0$? (Points 25%)
- c) What is the probability that at the time $t > 0$ the system is still in the state ψ_0 ? (Points 20%)

Problem 2

A *free* uni-dimensional particle of mass m is confined to the interval $[0, L]$ of the real line. The particle is, at the time $t = 0$, in the state described by the (non-normalized) wave function

$$\psi_0(x) = \sin \frac{\pi x}{L} + \sin \frac{2\pi x}{L} \quad (2)$$

- a) What is the average energy of this state at time $t > 0$? (Points 5%)
- b) What is the probability that at the time $t > 0$ the particle is in the region $0 < x < \frac{L}{4}$? (Points 15%)
- c) Compute the probability that at the time $t > 0$ the particle be in the state described by the wave function

$$\psi_1(x) = \sin \frac{\pi x}{L} - \sin \frac{2\pi x}{L} \quad (3)$$

(Points 10%)

Problem 3

Find the *normalized* radial wave function of the bound state of the hydrogenoid with angular momentum $l = 1$ and lowest possible energy, by looking for solutions of the radial Schrödinger equation with $l = 1$ of the form

$$\chi(\rho) = C \rho^2 e^{-A\rho} \quad (4)$$

where

$$\rho = \frac{Z r}{a_B} \quad (5)$$

Z is the atomic number, a_B the Bohr radius, r the radial coordinate, $\chi(r) = r R(r)$ with $R(r)$ the radial wave function, A and C are two numerical constants to be determined.

- a) Determine A , C and the eigenvalue E of the energy corresponding to this eigenfunction. (Points 15%)
- b) Explain why the eigenvalue E is the lowest possible with the given angular momentum. (Points 5%)

Problem 1

The norm squared of ψ_0 is

$$\langle \psi_0, \psi_0 \rangle = \frac{1}{2} + \frac{1}{2} + \frac{1}{5} = \frac{6}{5} \quad (6)$$

Let us consider the normalized state

$$\begin{aligned} \tilde{\psi}_0 &= \frac{\sqrt{5}}{\sqrt{6}} \left(\frac{1}{\sqrt{2}} |0\rangle + \frac{1}{\sqrt{2}} |1\rangle + \frac{1}{\sqrt{5}} |3\rangle \right) = \\ &= \frac{\sqrt{5}}{\sqrt{12}} |0\rangle + \frac{\sqrt{5}}{\sqrt{12}} |1\rangle + \frac{1}{\sqrt{6}} |3\rangle \end{aligned} \quad (7)$$

The normalized state at time t is

$$\tilde{\psi}_0(t) = e^{-i\frac{\omega}{2}t} \left(\frac{\sqrt{5}}{\sqrt{12}} |0\rangle + e^{-i\omega t} \frac{\sqrt{5}}{\sqrt{12}} |1\rangle + e^{-3i\omega t} \frac{1}{\sqrt{6}} |3\rangle \right) \quad (8)$$

The average of the energy is independent of time and is

$$\langle \tilde{\psi}_0, \hat{H} \tilde{\psi}_0 \rangle = \hbar \omega \left(\frac{1}{2} \times \frac{5}{12} + \frac{3}{2} \times \frac{5}{12} + \frac{7}{2} \times \frac{1}{6} \right) = \frac{17}{12} \hbar \omega \quad (9)$$

\hat{x} and \hat{p} can be expressed in terms of a and a^\dagger

$$\hat{x} = i\lambda (a - a^\dagger) \quad \hat{p} = \frac{\hbar}{2\lambda} (a + a^\dagger) \quad \lambda \equiv \sqrt{\frac{\hbar}{2m\omega}} \quad (10)$$

Therefore

$$\begin{aligned} \hat{x} \tilde{\psi}_0(t) &= i\lambda e^{-i\frac{\omega}{2}t} \left(-\frac{\sqrt{5}}{\sqrt{12}} |1\rangle + \frac{\sqrt{5}}{\sqrt{12}} e^{-i\omega t} |0\rangle - \frac{\sqrt{5}\sqrt{2}}{\sqrt{12}} e^{-i\omega t} |2\rangle + \right. \\ &\quad \left. + \frac{\sqrt{3}}{\sqrt{6}} e^{-3i\omega t} |2\rangle - \frac{\sqrt{4}}{\sqrt{6}} e^{-3i\omega t} |4\rangle \right) \end{aligned} \quad (11)$$

Therefore the average of \hat{x}^2 is

$$\begin{aligned} \langle \tilde{\psi}_0(t), \hat{x}^2 \tilde{\psi}_0(t) \rangle &= \langle \hat{x} \tilde{\psi}_0, \hat{x} \tilde{\psi}_0 \rangle = \lambda^2 \left(\frac{5}{12} + \frac{5}{12} + \frac{5}{6} \left| 1 - \frac{\sqrt{3}}{\sqrt{5}} e^{-2i\omega t} \right|^2 + \right. \\ &\quad \left. + \frac{4}{6} \right) = \lambda^2 \left[\frac{3}{2} + \frac{5}{6} \left(1 + \frac{3}{5} - \frac{2\sqrt{3}}{\sqrt{5}} \cos(2\omega t) \right) \right] = \\ &= \lambda^2 \left[\frac{17}{6} - \frac{\sqrt{5}}{\sqrt{3}} \cos(2\omega t) \right] \end{aligned} \quad (12)$$

The probability amplitude to be in the state ψ_0 at the time t

$$\langle \tilde{\psi}_0, \tilde{\psi}_0(t) \rangle = e^{\frac{-i\omega t}{2}} \left[\frac{5}{12} + \frac{5}{12} e^{-i\omega t} + \frac{1}{6} e^{-3i\omega t} \right] \quad (13)$$

The corresponding probability is

$$\begin{aligned} P(t) &= |\langle \tilde{\psi}_0, \tilde{\psi}_0(t) \rangle|^2 = \left| \frac{5}{12} + \frac{5}{12} e^{-i\omega t} + \frac{1}{6} e^{-3i\omega t} \right|^2 = \\ &= \frac{1}{12^2} \left| 5 + 5 e^{-i\omega t} + 2 e^{-3i\omega t} \right|^2 = \\ &= \frac{1}{12^2} \left[54 + 50 \cos(\omega t) + 20 \cos(2\omega t) + 20 \cos(3\omega t) \right] = \\ &= \frac{1}{72} \left[27 + 25 \cos(\omega t) + 10 \cos(2\omega t) + 10 \cos(3\omega t) \right] \end{aligned} \quad (14)$$

Of course

$$P(0) = 1 \quad (15)$$

This function is periodic with period $T = \frac{2\pi}{\omega}$. Therefore at the times

$$t_n = \frac{2\pi n}{\omega} \quad (16)$$

the probability $P(t)$ equals one

$$P(t_n) = 1 \quad (17)$$

Problem 2

The eigenvalues of the energy of the system are

$$E_n = \frac{n^2 \hbar^2 \pi^2}{2mL^2} \quad n = 1, 2, \dots \quad (18)$$

Since $\psi_0(x)$ is the sum of the two eigenfunctions with energies E_1 and E_2 the average energy is

$$\langle H \rangle = \frac{1}{2} (E_1 + E_2) = \frac{5 \hbar^2 \pi^2}{4mL^2} \quad (19)$$

This is also the average energy at the time t , since the average of the energy does not depend on time.

Let us compute the norm of the wave function

$$\begin{aligned}\langle \psi_0, \psi_0 \rangle &= \int_0^L dx \left(\sin \frac{\pi x}{L} + \sin \frac{2\pi x}{L} \right)^2 = \\ &= \int_0^L dx \left(\sin^2 \frac{\pi x}{L} + \sin^2 \frac{2\pi x}{L} \right) = \frac{L}{2} + \frac{L}{2} = L\end{aligned}\quad (20)$$

The *normalized* wave function at the time t is

$$\tilde{\psi}_0(x, t) = \frac{1}{\sqrt{L}} \left[e^{-i\frac{\hbar\pi^2 t}{2mL^2}} \sin \frac{\pi x}{L} + e^{-i\frac{2\hbar\pi^2 t}{mL^2}} \sin \frac{2\pi x}{L} \right] \quad (21)$$

The probability $P(t)$ that particle is in the interval $[0, \frac{L}{3}]$ at the time $t > 0$ is

$$\begin{aligned}P(t) &= \frac{1}{L} \int_0^{\frac{L}{3}} dx \left[\sin^2 \frac{\pi x}{L} + \sin^2 \frac{2\pi x}{L} + 2 \cos \frac{3\hbar\pi^2 t}{2mL^2} \sin \frac{\pi x}{L} \sin \frac{2\pi x}{L} \right] = \\ &= \int_0^{\frac{1}{3}} dy \left[\sin^2(\pi y) + \sin^2(2\pi y) + 2 \cos \frac{3\hbar\pi^2 t}{2mL^2} \sin(\pi y) \sin(2\pi y) \right] = \\ &= \left[\frac{1}{8} - \frac{1}{4\pi} + \frac{1}{8} + 2 \cos \frac{3\hbar\pi^2 t}{2mL^2} \left(\frac{1}{3\sqrt{2}\pi} \right) \right] = \\ &= \frac{1}{4} - \frac{1}{4\pi} + \frac{\sqrt{2}}{3\pi} \cos \frac{3\hbar\pi^2 t}{2mL^2}\end{aligned}\quad (22)$$

The normalized wave function corresponding to $\psi_1(x)$ is

$$\tilde{\psi}_1(x) = \frac{1}{\sqrt{L}} \left(\sin \frac{\pi x}{L} - \sin \frac{2\pi x}{L} \right) \quad (23)$$

The amplitude probability that at the time t the particle is in the state ψ_1 is

$$A_1(t) = \langle \tilde{\psi}_1, \tilde{\psi}_0(t) \rangle = \frac{1}{2} e^{-i\frac{\hbar\pi^2 t}{2mL^2}} - \frac{1}{2} e^{-i\frac{2\hbar\pi^2 t}{mL^2}} \quad (24)$$

The probability is

$$P_1(t) = |A_1(t)|^2 = \frac{1}{2} \left(1 - \cos \frac{3\hbar\pi^2 t}{2mL^2} \right) = \sin^2 \frac{3\hbar\pi^2 t}{2mL^2} \quad (25)$$

Problem 3

The Schrödinger equation for $\chi_{E,l}(\rho)$ of angular momentum l , written in adimensional variables is

$$-\chi_{E,l}''(\rho) + \left(-\frac{2}{\rho} + \frac{l(l+1)}{\rho^2}\right) \chi_{E,l}(\rho) = 2\epsilon \chi_{E,l}(\rho) \quad (26)$$

where ϵ is an adimensional quantity proportional to the energy

$$\epsilon = \frac{E}{\frac{Z^2 \hbar^2}{m a_B^2}} \quad (27)$$

For $l = 1$ this is

$$\frac{\chi_{E,1}''}{\chi_{E,1}} = -\frac{2}{\rho} + \frac{2}{\rho^2} - 2\epsilon \quad (28)$$

Using

$$\chi_{E,1}(\rho) = C \rho^2 e^{-A\rho} \quad (29)$$

we obtain

$$A^2 + \frac{2}{\rho^2} - \frac{4A}{\rho} = -\frac{2}{\rho} + \frac{2}{\rho^2} - 2\epsilon \quad (30)$$

Therefore we arrive to the equations

$$4A = 2 \quad A^2 = -2\epsilon \quad (31)$$

whose solution is

$$A = \frac{1}{2} \quad \epsilon = -\frac{1}{8} \quad (32)$$

This value of ϵ corresponds to the energy

$$E = -\frac{Z^2 \hbar^2}{2m a_B^2} \frac{1}{2^2} \quad (33)$$

which is indeed the Bohr level with $n = 2$.

The normalization factor C is determined from

$$\int_0^\infty d\rho \chi_{E,l}^2(\rho) = \frac{Z}{a_B} \quad (34)$$

From the expression (29) we obtain

$$C^2 \int_0^\infty d\rho \rho^4 e^{-\rho} = C^2 24 = \frac{Z}{a_B} \quad (35)$$

Hence

$$C = \sqrt{\frac{Z}{a_B} \frac{1}{2\sqrt{6}}} \quad (36)$$

Since the wave function has no nodes for $\rho > 0$ it must correspond to the lowest energy eigenvalue with the given l .

Quantum Mechanics: SERP-CHEM
Final written test: 28/1/2013

Problem 1

A quantum system is described by a 3-dimensional space of states. Let $\{|1\rangle, |2\rangle, |3\rangle\}$ be an orthonormal base and let the Hamiltonian of the system in this base be

$$H = \begin{pmatrix} \epsilon & \eta & \eta \\ \eta & \epsilon & \eta \\ \eta & \eta & \epsilon \end{pmatrix} \quad (37)$$

where ϵ and η are real parameters.

- a) Show that the operator represented in the given basis by the matrix

$$T = \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix} \quad (38)$$

commutes with the Hamiltonian H . Does T correspond to an observable? (Points 10%)

- b) Compute the eigenvectors and eigenvalues of T . (Points 20%)
- c) Using (b), determine the eigenvectors and eigenvalues of H . (Points 25%)
- d) Suppose that at the time $t = 0$ the system is in the state $\psi_0 = |1\rangle$. What is the probability that the system is again in the same state $|1\rangle$ after a time t ? (Points 20%)

Problem 2

An harmonic oscillator of frequency ω is, at time $t = 0$, in the state

$$\psi_0 = |2\rangle + 2|3\rangle \quad (39)$$

- a) Compute the average of \hat{x} and \hat{x}^2 at the time t . (Points 15%)
- b) Write the normalized wave function of the state at the time t in the Schrödinger representation. (Points 10%)

Problem 1

a)

$$\begin{aligned} HT &= \begin{pmatrix} \epsilon & \eta & \eta \\ \eta & \epsilon & \eta \\ \eta & \eta & \epsilon \end{pmatrix} \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix} = \begin{pmatrix} \eta & \epsilon & \eta \\ \eta & \eta & \epsilon \\ \epsilon & \eta & \eta \end{pmatrix} \\ TH &= \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix} \begin{pmatrix} \epsilon & \eta & \eta \\ \eta & \epsilon & \eta \\ \eta & \eta & \epsilon \end{pmatrix} = \begin{pmatrix} \eta & \epsilon & \eta \\ \eta & \eta & \epsilon \\ \epsilon & \eta & \eta \end{pmatrix} \end{aligned} \quad (40)$$

T is not hermitian, and thus it does not correspond to an observable.

b)

The eigenvalues of T are given by the secular equation

$$P(t) = \det \begin{pmatrix} -t & 1 & 0 \\ 0 & -t & 1 \\ 1 & 0 & -t \end{pmatrix} = -t(t^2) - 1(-1) = 0 \quad (41)$$

Hence

$$t_1 = e^{\frac{2\pi}{3}i} \quad t_2 = t_1^2 = t_1^{-1} \quad t_3 = t_1^3 = 1 \quad (42)$$

The eigenvectors relative to t_k ,

$$v_k = \begin{pmatrix} x \\ y \\ z \end{pmatrix} \quad \text{with } k = 1, 2, 3, \quad (43)$$

satisfy the equations

$$y = t_k x \quad z = t_k y = t_k^2 z \quad (44)$$

Hence the normalized eigenvectors are

$$v_k = \frac{1}{\sqrt{3}} \begin{pmatrix} 1 \\ t_k \\ t_k^2 \end{pmatrix} \quad \text{with } k = 1, 2, 3 \quad (45)$$

or, explicitly

$$v_1 = \frac{1}{\sqrt{3}} \begin{pmatrix} 1 \\ t_1 \\ t_1^{-1} \end{pmatrix} \quad v_2 = \frac{1}{\sqrt{3}} \begin{pmatrix} 1 \\ t_1^{-1} \\ t_1 \end{pmatrix} \quad v_3 = \frac{1}{\sqrt{3}} \begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix} \quad (46)$$

c) Consider:

$$T v_k = t_k v_k \quad (47)$$

Then

$$H T v_k = t_k H v_k \quad (48)$$

Since H and T commute, we obtain

$$T (H v_k) = t_k (H v_k) \quad (49)$$

Therefore $H v_k$ is an eigenvector of T with eigenvalue t_k . Since t_k is non-degenerate and its only eigenvector is v_k , $H v_k$ must be proportional to v_k :

$$H v_k = E_k v_k \quad (50)$$

Thus, v_k are simultaneous eigenvectors of H and T . We can compute the eigenvalues E_k by acting on v_k with H

$$H v_1 = \begin{pmatrix} \epsilon & \eta & \eta \\ \eta & \epsilon & \eta \\ \eta & \eta & \epsilon \end{pmatrix} \frac{1}{\sqrt{3}} \begin{pmatrix} 1 \\ t_1 \\ t_1^{-1} \end{pmatrix} = \frac{1}{\sqrt{3}} \begin{pmatrix} 1 \\ t_1 \\ t_1^{-1} \end{pmatrix} (\epsilon + \eta(t_1 + t_1^{-1})) \quad (51)$$

Thus

$$E_1 = \epsilon + \eta(t_1 + t_1^{-1}) = \epsilon + 2\eta \cos \frac{2\pi}{3} = \epsilon - \eta \quad (52)$$

Analogously

$$H v_2 = \begin{pmatrix} \epsilon & \eta & \eta \\ \eta & \epsilon & \eta \\ \eta & \eta & \epsilon \end{pmatrix} \frac{1}{\sqrt{3}} \begin{pmatrix} 1 \\ t_1^{-1} \\ t_1 \end{pmatrix} = \frac{1}{\sqrt{3}} \begin{pmatrix} 1 \\ t_1^{-1} \\ t_1 \end{pmatrix} (\epsilon + \eta(t_1^{-1} + t_1)) \quad (53)$$

from which

$$E_2 = E_1 = \epsilon - \eta \quad (54)$$

Finally

$$H v_3 = \begin{pmatrix} \epsilon & \eta & \eta \\ \eta & \epsilon & \eta \\ \eta & \eta & \epsilon \end{pmatrix} \frac{1}{\sqrt{3}} \begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix} = \frac{1}{\sqrt{3}} \begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix} (\epsilon + 2\eta) \quad (55)$$

and

$$E_3 = \epsilon + 2\eta \quad (56)$$

d) Let us decompose the state $|1\rangle$ in the base $\{v_1, v_2, v_3\}$:

$$\begin{aligned} |1\rangle &= v_1 \langle v_1|1\rangle + v_2 \langle v_2|1\rangle + v_3 \langle v_3|1\rangle = \\ &= \frac{1}{\sqrt{3}} (v_1 + v_2 + v_3) \end{aligned} \quad (57)$$

Hence the state at the time t is

$$\begin{aligned} \psi(t) &= \frac{1}{\sqrt{3}} e^{-\frac{i E_1 t}{\hbar}} (v_1 + v_2 + e^{-\frac{i(E_3 - E_1)t}{\hbar}} v_3) = \\ &= \frac{1}{\sqrt{3}} e^{-\frac{i E_1 t}{\hbar}} (v_1 + v_2 + e^{-\frac{i 3\eta t}{\hbar}} v_3) \end{aligned} \quad (58)$$

The amplitude for this state to be into the state $|1\rangle$ is

$$A(t) = \langle 1|\psi(t)\rangle = \frac{1}{3} e^{-\frac{i E_1 t}{\hbar}} (2 + e^{-\frac{i 3\eta t}{\hbar}}) \quad (59)$$

The corresponding probability

$$P(t) = |A(t)|^2 = \frac{1}{9} \left(5 + 4 \cos \frac{3\eta t}{\hbar} \right) \quad (60)$$

Problem 2

a)

Let us write \hat{x} in terms of a and a^\dagger

$$\hat{x} = i \lambda (a - a^\dagger) \quad \lambda = \sqrt{\frac{\hbar}{2m\omega}} \quad (61)$$

The system is at the time t in the state described by the normalized vector

$$\psi(t) = \frac{1}{\sqrt{5}} e^{-i\frac{5}{2}\omega t} (|2\rangle + 2 e^{-i\omega t} |3\rangle) \quad (62)$$

Hence

$$\hat{x} \psi(t) = \frac{i\lambda}{\sqrt{5}} e^{-i\frac{5}{2}\omega t} (\sqrt{2}|1\rangle - \sqrt{3}|3\rangle + 2\sqrt{3}e^{-i\omega t}|2\rangle - 4e^{-i\omega t}|4\rangle) \quad (63)$$

Therefore

$$\langle \psi(t) | \hat{x} | \psi(t) \rangle = \frac{i\lambda}{5} (2\sqrt{3}e^{-i\omega t} - 2\sqrt{3}e^{i\omega t}) = \frac{4\sqrt{3}\lambda}{5} \sin \omega t \quad (64)$$

and

$$\langle \psi(t) | \hat{x}^2 | \psi(t) \rangle = \langle \hat{x} \psi(t), \hat{x} \psi(t) \rangle = \frac{\lambda^2}{5} (2 + 3 + 12 + 16) = \frac{33\lambda^2}{5} \quad (65)$$

b) The state at the time t is

$$\psi(t) = \frac{1}{\sqrt{5}} e^{-i\frac{5}{2}\omega t} (|2\rangle + 2e^{-i\omega t}|3\rangle) \quad (66)$$

The normalized wave function of the ground state in the Schrödinger representation is

$$\psi_0(x) = \frac{1}{(2\pi)^{\frac{1}{4}} \lambda^{\frac{1}{2}}} e^{-\frac{x^2}{4\lambda^2}} = \frac{1}{(2\pi)^{\frac{1}{4}} \lambda^{\frac{1}{2}}} e^{-\frac{y^2}{4}} \quad y \equiv \frac{x}{\lambda} \quad (67)$$

Therefore the normalized wave function of the first excited state is

$$\begin{aligned} \psi_1(x) &= -i \left(\lambda \frac{d}{dx} - \frac{1}{2} \frac{x}{\lambda^2} \right) \psi_0(x) = -i \left(\frac{d}{dy} - \frac{1}{2} y \right) \psi_0 = \\ &= -i \left(-\frac{1}{2} y - \frac{1}{2} y \right) \psi_0 = i y \psi_0 \end{aligned} \quad (68)$$

and

$$\begin{aligned} \psi_2(x) &= \frac{1}{\sqrt{2}} \left(\frac{d}{dy} - \frac{1}{2} y \right) y \psi_0 = \frac{1}{\sqrt{2}} (-y^2 \psi_0 + \psi_0) = \frac{1}{\sqrt{2}} (1 - y^2) \psi_0 \\ \psi_3(x) &= \frac{-i}{\sqrt{6}} \left(\frac{d}{dy} - \frac{1}{2} y \right) ((1 - y^2) \psi_0) = \\ &= \frac{-i}{\sqrt{6}} [-(1 - y^2) y \psi_0 - 2y \psi_0] = \frac{-i}{\sqrt{6}} [y^3 - 3y] \psi_0 \end{aligned} \quad (69)$$

Therefore the normalized wave-function of the state at the time t is

$$\begin{aligned} \psi(x, t) &= \frac{1}{\sqrt{5}} e^{-i\frac{5}{2}\omega t} \left(\frac{1}{\sqrt{2}} (1 - y^2) - \frac{2i e^{-i\omega t}}{\sqrt{6}} (y^3 - 3y) \right) \psi_0 = \\ &= \frac{e^{-i\frac{5}{2}\omega t}}{\sqrt{5} (2\pi)^{\frac{1}{4}} \lambda^{\frac{1}{2}}} \left(\frac{1}{\sqrt{2}} (1 - y^2) - \frac{2i e^{-i\omega t}}{\sqrt{6}} (y^3 - 3y) \right) e^{-\frac{y^2}{4}} \end{aligned} \quad (70)$$

Quantum Mechanics: SERP-CHEM
Final written test: 12/7/2013

Problem 1

A quantum system is described by a 2-dimensional space of states. Let $\{|1\rangle, |2\rangle\}$ be an orthonormal base and let the Hamiltonian of the system in this base be

$$H = \begin{pmatrix} a & b \\ b^* & a \end{pmatrix} \quad (71)$$

where a and b are *complex* numbers.

- a) What are the restriction on the numbers a and b for H to be hermitian? (Points 10%)
- b) Compute the eigenvalues and the normalized eigenvectors of H , when H is hermitian. (Points 20%)
- c) Suppose that the system be at the time $t = 0$ in the state $|1\rangle$:

$$\psi(0) = |1\rangle \quad (72)$$

Compute the probability at the time t that the system be in the state $|2\rangle$. (Points 25%)

Problem 2

An otherwise free one-dimensional particle of mass m is confined to a box of size L . Let us denote by $|E_n\rangle$ the eigenstates of the energy, with $n = 1, 2, 3, \dots$

- a) What is the normalized wave function of the fundamental state in the *momentum representation*? (Points 20%)
- b) What is the normalized distribution probability of the momentum when the particle is in the fundamental state? (Points 10%)
- c) What is the average of \hat{p}^2 in the fundamental state? (Points 10%)
- d) Suppose the particle is in the state $\psi(0) = |E_1\rangle + 3i|E_2\rangle$ at the time $t = 0$. What is the smallest probability that the particle be in the state $\psi(0)$ at any time $t > 0$? (Points 15%)

Problem 1

- a) The hermitian conjugate of H is

$$H^\dagger = \begin{pmatrix} a^* & b \\ b^* & a^* \end{pmatrix} \quad (73)$$

Therefore the condition for H to be hermitian is

$$a = a^* \quad (74)$$

i.e. a real.

- b) The eigenvalues are determined by the equation

$$\begin{aligned} 0 &= \det(H - E\mathbb{I}) = \det \begin{pmatrix} a - E & b \\ b^* & a - E \end{pmatrix} = \\ &= E^2 - 2aE + a^2 - |b|^2 \end{aligned} \quad (75)$$

that is

$$E = E_\pm = a \pm |b| \quad (76)$$

The corresponding eigenvectors

$$|E_\pm\rangle = x_\pm|1\rangle + y_\pm|2\rangle \quad (77)$$

are determined by the equations

$$\begin{pmatrix} a - E_\pm & b \\ b^* & a - E_\pm \end{pmatrix} \begin{pmatrix} x_\pm \\ y_\pm \end{pmatrix} = 0 \quad (78)$$

that is

$$(a - E_\pm)x_\pm = -by_\pm \quad (79)$$

that is

$$\mp |b|x_\pm = -by_\pm \Rightarrow x_\pm = \pm \frac{b}{|b|} y_\pm = \pm e^{i\theta_b} y_\pm \quad (80)$$

where θ_b is the argument of b

$$b = |b| e^{i\theta_b} \quad (81)$$

Thus the normalized eigenvectors are

$$|E_{\pm}\rangle = \frac{1}{\sqrt{2}} (\pm e^{i\theta_b} |1\rangle + |2\rangle) \quad (82)$$

- c) Let us decompose $|1\rangle$ in the basis $\{|E_+\rangle, |E_-\rangle\}$:

$$\psi(0) = |1\rangle = \frac{1}{\sqrt{2}} e^{-i\theta_b} (|E_+\rangle - |E_-\rangle) \quad (83)$$

The state at the time t is therefore

$$\begin{aligned} \psi(t) &= \frac{1}{\sqrt{2}} e^{-i\theta_b} (e^{-i\frac{E_+}{\hbar}t} |E_+\rangle - e^{-i\frac{E_-}{\hbar}t} |E_-\rangle) = \\ &= \frac{1}{\sqrt{2}} e^{-i\theta_b} e^{-i\frac{a}{\hbar}t} (e^{-i\frac{|b|}{\hbar}t} |E_+\rangle - e^{i\frac{|b|}{\hbar}t} |E_-\rangle) \end{aligned} \quad (84)$$

The amplitude to be in the state $|2\rangle$ at the time t is therefore

$$\begin{aligned} A_{1\rightarrow 2}(t) &= \langle 2|\psi(t)\rangle = \frac{1}{\sqrt{2}} e^{-i\theta_b} e^{-i\frac{a}{\hbar}t} (e^{-i\frac{|b|}{\hbar}t} \langle 2|E_+\rangle + \\ &\quad - e^{i\frac{|b|}{\hbar}t} \langle 2|E_-\rangle) = \\ &= \frac{1}{2} e^{-i\theta_b} e^{-i\frac{a}{\hbar}t} (e^{-i\frac{|b|}{\hbar}t} - e^{i\frac{|b|}{\hbar}t}) = \\ &= i e^{-i\theta_b} e^{-i\frac{a}{\hbar}t} \sin \frac{|b|}{\hbar} t \end{aligned} \quad (85)$$

and the probability

$$P_{1\rightarrow 2}(t) = |A_{1\rightarrow 2}(t)|^2 = \sin^2 \frac{|b|}{\hbar} t \quad (86)$$

Remark: By changing basis, and using $|1'\rangle = e^{i\theta_b} |1\rangle$ and $|2'\rangle = |2\rangle$, we can always change the matrix H to a *real* matrix

$$H' = \begin{pmatrix} a & |b| \\ |b| & a \end{pmatrix} \quad (87)$$

Therefore physical quantities cannot depend on the phase θ_b .

Problem 2

- a) The normalized wave function in the coordinate representation is

$$\psi_1(x) = \sqrt{\frac{2}{L}} \sin \frac{\pi x}{L} \quad (88)$$

if x is the coordinate in the interval $[0, L]$. The wave function in the momentum representation is

$$\begin{aligned} \tilde{\psi}_1(p) &= \int_0^L \psi_1(x) e^{-i \frac{p}{\hbar} x} \frac{dx}{\sqrt{2\pi\hbar}} = \\ &= \int_0^L \left[e^{i(\frac{\pi}{L} - \frac{p}{\hbar})x} - e^{-i(\frac{\pi}{L} + \frac{p}{\hbar})x} \right] \frac{dx}{2i\sqrt{\pi\hbar L}} = \\ &= \left[\frac{e^{i(\frac{\pi}{L} - \frac{p}{\hbar})L} - 1}{\frac{\pi}{L} - \frac{p}{\hbar}} + \frac{e^{-i(\frac{\pi}{L} + \frac{p}{\hbar})L} - 1}{\frac{\pi}{L} + \frac{p}{\hbar}} \right] \frac{-1}{2\sqrt{\pi\hbar L}} = \\ &= \frac{\frac{\pi}{L}}{\frac{\pi^2}{L^2} - \frac{p^2}{\hbar^2}} \frac{e^{-i \frac{p}{\hbar} L} + 1}{\sqrt{\pi\hbar L}} = \frac{e^{-i \frac{p}{\hbar} L} + 1}{\frac{\hbar^2 \pi^2}{L^2} - p^2} \sqrt{\frac{\pi\hbar^3}{L^3}} \end{aligned} \quad (89)$$

- b) The probability distribution of the momentum is therefore

$$|\tilde{\psi}_1(p)|^2 = \frac{|e^{-i \frac{p}{\hbar} L} + 1|^2}{(\frac{\hbar^2 \pi^2}{L^2} - p^2)^2} \frac{\pi\hbar^3}{L^3} = \frac{\cos^2(\frac{p}{2\hbar} L)}{(\frac{\hbar^2 \pi^2}{L^2} - p^2)^2} \frac{4\pi\hbar^3}{L^3} \quad (90)$$

- c) $\psi_1(x)$ is an eigenfunction of \hat{p}^2 , therefore the average of \hat{p}^2 on this state is its eigenvalue

$$\langle \psi_1, \hat{p}^2 \psi_1 \rangle = \frac{\hbar^2 \pi^2}{L^2} \quad (91)$$

- d) The normalized state at the time t is

$$\psi(t) = \frac{1}{\sqrt{10}} e^{-it \frac{E_1}{\hbar}} |E_1\rangle + \frac{3}{\sqrt{10}} i e^{-it \frac{E_2}{\hbar}} |E_2\rangle \quad (92)$$

The amplitude to be in the same state $\psi(0)$ at the time t is

$$\langle \frac{1}{\sqrt{10}} \psi(0), \psi(t) \rangle = \frac{1}{10} e^{-it \frac{E_1}{\hbar}} + \frac{9}{10} e^{-it \frac{E_2}{\hbar}} \quad (93)$$

The corresponding probability is

$$\begin{aligned} P(t) &= \left| \left\langle \frac{1}{\sqrt{10}} \psi(0), \psi(t) \right\rangle \right|^2 = \frac{82}{100} + \frac{18}{100} \cos \frac{E_2 - E_1}{\hbar} t = \\ &= \frac{82}{100} + \frac{18}{100} \cos \frac{3\pi^2 \hbar t}{2mL^2} \end{aligned} \quad (94)$$

The smallest probability to be in the fundamental state is therefore

$$P_{min} = \frac{82}{100} - \frac{18}{100} = \frac{64}{100} \quad (95)$$

Quantum Mechanics: SERP-CHEM
Final written test: 7/1/2014

Problem 1

An harmonic oscillator of frequency ω and mass m is in the state

$$\psi = |0\rangle + i|1\rangle$$

- a) Compute the *normalized* wave function of the state in the *momentum* representation. (Points 20%)
- b) Compute the average value on this state of the operator $\hat{O} = \hat{x}\hat{p} + \hat{p}\hat{x}$. (Points 20%)
- c) Compute the average of \hat{O} at the time t . (Points 20%)

Problem 2

A quantum system is described by a 2-dimensional space of states. In the base $\{|1\rangle, |2\rangle\}$ the Hamiltonian of the system corresponds to the following matrix

$$H = \begin{pmatrix} a & b \\ b & 3a \end{pmatrix}$$

where a and b are *real* numbers.

- a) What are the normalized energy eigenstates and energy eigenvalues of the system? (Points 20%)
- b) Suppose that the system be at the time $t = 0$ in the state $\psi(0) = |1\rangle$. What is the probability $P(t)$ that the system is in the ground state at the time $t > 0$? (Points 20%)
- c) Suppose that the system above is used to describe a molecule made up of two different atoms (or sub-molecules) with two bonding electrons¹. What is the ground state energy of the molecule in the independent electron approximation and its binding energy? (Points 30%)

¹*Reminder:* In this schematization, when the two atoms are separated one of the two valence electrons is attached to the first atom (state $|1\rangle$) while the other electron localized around the second atom (state $|2\rangle$). When the two atoms get closer, b becomes non-vanishing and the valence electrons can be shared by the two atoms (or sub-molecules).

Problem 1

a) The *normalized* state is

$$\psi' = \frac{1}{\sqrt{2}} |0\rangle + i \frac{1}{\sqrt{2}} |1\rangle$$

The ground state satisfies the equation

$$a |0\rangle = (\hat{p} - i m \omega \hat{x}) |0\rangle = 0$$

In the momentum representation this becomes

$$m \omega \hbar \frac{d\tilde{\psi}_0(p)}{dp} = -p \tilde{\psi}_0(p)$$

where $\tilde{\psi}_0(p)$ is the wave function of the ground state $|0\rangle$ in the momentum representation. The solution of this differential equation is

$$\tilde{\psi}_0(p) = C e^{-\frac{p^2}{2m\omega\hbar}}$$

The normalization factor C is fixed by

$$1 = \int_{-\infty}^{\infty} dp |\tilde{\psi}_0(p)|^2 = |C|^2 \int_{-\infty}^{\infty} dp e^{-\frac{p^2}{m\omega\hbar}} = |C|^2 \sqrt{\pi} \sqrt{m\omega\hbar}$$

We can therefore take

$$\tilde{\psi}_0(p) = \frac{1}{(\pi m \omega \hbar)^{\frac{1}{4}}} e^{-\frac{p^2}{2m\omega\hbar}} = \frac{2^{\frac{1}{4}}}{(\pi)^{\frac{1}{4}}} \frac{\sqrt{\lambda}}{\sqrt{\hbar}} e^{-\frac{\lambda^2 p^2}{\hbar^2}}$$

where $\lambda = \sqrt{\frac{\hbar}{2\omega m}}$. The first excited state is obtain from

$$|1\rangle = a^\dagger |0\rangle = \frac{\lambda}{\hbar} (\hat{p} + i m \omega \hat{x}) |0\rangle$$

Hence

$$\begin{aligned} \tilde{\psi}_1(p) &= C \frac{\lambda}{\hbar} \left(p - m \omega \hbar \frac{d}{dp} \right) e^{-\frac{p^2}{2m\omega\hbar}} = \\ &= C \frac{\lambda}{\hbar} (p + p) e^{-\frac{p^2}{2m\omega\hbar}} = C \frac{2p\lambda}{\hbar} e^{-\frac{p^2}{2m\omega\hbar}} \end{aligned}$$

In conclusion the normalized wave function of ψ in the momentum representation is

$$\tilde{\psi}(p) = \frac{C}{\sqrt{2}} \left(1 + i \frac{2p\lambda}{\hbar}\right) e^{-\frac{p^2}{2m\omega\hbar}} = \frac{1}{(2\pi)^{\frac{1}{4}}} \frac{\sqrt{\lambda}}{\sqrt{\hbar}} \left(1 + i \frac{2p\lambda}{\hbar}\right) e^{-\frac{\lambda^2 p^2}{\hbar^2}}$$

b) Let us write \hat{O} in terms of a and a^\dagger :

$$\begin{aligned} \hat{O} &= \hat{x}\hat{p} + \hat{p}\hat{x} = \frac{\hbar^2}{4\lambda^2} \frac{i}{m\omega} [(a + a^\dagger)(a - a^\dagger) + (a - a^\dagger)(a + a^\dagger)] = \\ &= \frac{\hbar^2}{4\lambda^2} \frac{i}{m\omega} [(a + a^\dagger)(a - a^\dagger) + (a - a^\dagger)(a + a^\dagger)] = i\hbar [a^2 - (a^\dagger)^2] \end{aligned}$$

Then

$$\begin{aligned} \langle \psi, \hat{O}\psi \rangle &= i\hbar \langle \psi, [a^2 - (a^\dagger)^2](|0\rangle + i|1\rangle) \rangle = \\ &= -i\hbar \langle \psi, (\sqrt{2}|2\rangle + i\sqrt{6}|3\rangle) \rangle = 0 \end{aligned}$$

Hence the average of \hat{O} on this state is zero.

c) At the time t , the state is

$$\psi(t) = e^{-i\frac{\omega t}{2}} (|0\rangle + i e^{-i\omega t} |1\rangle)$$

Hence

$$\begin{aligned} \langle \psi(t), \hat{O}\psi(t) \rangle &= e^{-i\frac{\omega t}{2}} i\hbar \langle \psi(t), [a^2 - (a^\dagger)^2](|0\rangle + i e^{-i\omega t} |1\rangle) \rangle = \\ &= -i\hbar e^{-i\frac{\omega t}{2}} \langle \psi, (\sqrt{2}|2\rangle + i\sqrt{6} e^{-i\omega t} |3\rangle) \rangle = 0 \end{aligned}$$

This means that the average of the operator vanishes for any time t .

Problem 2

a)

Energy eigenvalues E are given by the solutions of the equation

$$0 = \det \begin{pmatrix} a - E & b \\ b & 3a - E \end{pmatrix} = E^2 - 4aE + 3a^2 - b^2$$

Thus

$$E_{1,2} = 2a \pm \sqrt{a^2 + b^2}$$

The corresponding eigenvectors $\psi_{1,2} = \begin{pmatrix} x_{1,2} \\ y_{1,2} \end{pmatrix}$ are (for $b \neq 0$)

$$\psi_{1,2} = C_{1,2} \begin{pmatrix} b \\ E_{1,2} - a \end{pmatrix} = C_{1,2} \begin{pmatrix} b \\ a \pm \sqrt{a^2 + b^2} \end{pmatrix}$$

The normalized eigenvectors are determined by the condition

$$1 = |C_{1,2}|^2 2(a^2 + b^2 \pm a\sqrt{a^2 + b^2})$$

which means

$$|C_{1,2}|^2 = \frac{1}{2\sqrt{a^2 + b^2}} \frac{1}{\sqrt{a^2 + b^2} \pm a}$$

The ground state is ψ_2 since $E_2 < E_1$ for any value of a and b .

b) The state $|1\rangle$ writes in the basis $\{\psi_1, \psi_2\}$

$$|1\rangle = C_1 b \psi_1 + C_2 b \psi_2$$

The state at the time t is

$$\psi(t) = e^{-i\frac{E_1 t}{\hbar}} C_1 b \psi_1 + e^{-i\frac{E_2 t}{\hbar}} C_2 b \psi_2$$

The probability that at the time t the system is in the ground state ψ_2 is independent of t and is

$$P(t) = |C_2|^2 b^2 = \frac{b^2}{2\sqrt{a^2 + b^2}} \frac{1}{\sqrt{a^2 + b^2} - a}$$

c) The ground state of the molecule is the one in which both electrons occupy the level E_2 , therefore the energy of the ground state of the molecule is

$$E = 2 E_2 = 4 a - 2 \sqrt{a^2 + b^2}$$

The energy of the molecule when the electrons are each around its own atom is

$$E_0 = 3 a + a = 4 a$$

The binding energy is therefore

$$E_{binding} = E - E_0 = 2 \sqrt{a^2 + b^2}$$

Quantum Mechanics: SERP-CHEM
Final written test: 27/1/2014

Problem 1

Consider the state ψ of an harmonic oscillator of frequency ω and mass m which satisfies the equation

$$a \psi = \alpha \psi \tag{96}$$

where α is a *complex number*.

a) Find the *normalized* wave function of ψ in the Schrödinger representation. (Points 20%)

b) Compute Δx and Δp on the state ψ and show it is a state of minimal indeterminacy. (Points 20%)

c) Consider the state

$$\tilde{\psi} = \sum_{n=0}^{\infty} \frac{\alpha^n}{\sqrt{n!}} |n\rangle \tag{97}$$

where $|n\rangle$ with $n = 0, 1, 2, \dots$ are the normalized eigenstates of the harmonic oscillator Hamiltonian. Show that $\tilde{\psi}$ satisfies (96). (Points 20%)

d) Compute the norm of $\tilde{\psi}$. (Points 20%)

Problem 2

Consider the homogenous polynomial of degree 3

$$P(x, y, z) = x y z$$

a) Show that $P(x, y, z)$ harmonic. (Points 10%)

b) Decompose $P(x, y, z)$ as linear combination of harmonic polynomials $H_{3,m}(x, y, z)$ of definite L_3 eigenvalues. (Points 20%)

Problem 1

Solution:

a) The wave-function $\psi(x)$ satisfies the differential equation

$$-i \hbar \psi'(x) - i m \omega x \psi(x) = \frac{\hbar \alpha}{\lambda} \psi(x) \quad (98)$$

that is

$$\frac{\psi'(x)}{\psi(x)} = \frac{i \alpha}{\lambda} - \frac{x}{2 \lambda^2} \quad (99)$$

The solution is

$$\psi(x) = C e^{i \alpha \frac{x}{\lambda} - \frac{x^2}{4 \lambda^2}} \quad (100)$$

The normalized wave-function is obtained by imposing

$$\begin{aligned} 1 = \langle \psi, \psi \rangle &= |C|^2 \int_{-\infty}^{\infty} dx e^{i(\alpha - \bar{\alpha}) \frac{x}{\lambda} - \frac{x^2}{2 \lambda^2}} = |C|^2 \lambda \int_{-\infty}^{\infty} dy e^{i(\alpha - \bar{\alpha}) y - \frac{y^2}{2}} = \\ &= |C|^2 \lambda \sqrt{2 \pi} e^{-\frac{(\alpha - \bar{\alpha})^2}{2}} \end{aligned} \quad (101)$$

Hence

$$\psi(x) = \frac{1}{(2 \pi)^{\frac{1}{4}}} \frac{1}{\lambda^{\frac{1}{2}}} e^{\frac{(\alpha - \bar{\alpha})^2}{4}} e^{i \alpha \frac{x}{\lambda} - \frac{x^2}{4 \lambda^2}} \quad (102)$$

b) Let us compute Δx by making use of the Schrödinger representation:

$$\begin{aligned} \langle \psi, \hat{x} \psi \rangle &= |C|^2 \int_{-\infty}^{\infty} dx x e^{i(\alpha - \bar{\alpha}) \frac{x}{\lambda} - \frac{x^2}{2 \lambda^2}} = |C|^2 \lambda^2 \int_{-\infty}^{\infty} dy y e^{i(\alpha - \bar{\alpha}) y - \frac{y^2}{2}} = \\ &= -i |C|^2 \lambda^2 \sqrt{2 \pi} \frac{\partial}{\partial(\alpha - \bar{\alpha})} e^{-\frac{(\alpha - \bar{\alpha})^2}{2}} = \\ &= i |C|^2 \lambda^2 \sqrt{2 \pi} (\alpha - \bar{\alpha}) e^{-\frac{(\alpha - \bar{\alpha})^2}{2}} = i (\alpha - \bar{\alpha}) \lambda \end{aligned} \quad (103)$$

and

$$\begin{aligned} \langle \psi, \hat{x}^2 \psi \rangle &= |C|^2 \int_{-\infty}^{\infty} dx x^2 e^{i(\alpha - \bar{\alpha}) \frac{x}{\lambda} - \frac{x^2}{2 \lambda^2}} = |C|^2 \lambda^3 \int_{-\infty}^{\infty} dy y^2 e^{i(\alpha - \bar{\alpha}) y - \frac{y^2}{2}} = \\ &= -|C|^2 \lambda^3 \sqrt{2 \pi} \frac{\partial^2}{\partial(\alpha - \bar{\alpha})^2} e^{-\frac{(\alpha - \bar{\alpha})^2}{2}} = \\ &= |C|^2 \lambda^3 \sqrt{2 \pi} (1 - (\alpha - \bar{\alpha})^2) e^{-\frac{(\alpha - \bar{\alpha})^2}{2}} = \lambda^2 (1 - (\alpha - \bar{\alpha})^2) \end{aligned} \quad (104)$$

Thus

$$\Delta x^2 = \lambda^2 [1 - (\alpha - \bar{\alpha})^2 + (\alpha - \bar{\alpha})^2] = \lambda^2 \quad (105)$$

For Δp , let us show how to perform the computation by using raising and lowering operators together with Eq. (96). As a matter of fact, this method is simpler:

$$\begin{aligned} \langle \psi, \hat{p} \psi \rangle &= \frac{\hbar}{2\lambda} \langle \psi, (a + a^\dagger) \psi \rangle = \frac{\hbar}{2\lambda} \langle \psi, (\alpha + a^\dagger) \psi \rangle = \\ &= \frac{\hbar}{2\lambda} (\alpha + \langle a \psi, \psi \rangle) = \frac{\hbar}{2\lambda} (\alpha + \bar{\alpha}) \end{aligned} \quad (106)$$

And

$$\begin{aligned} \langle \psi, \hat{p}^2 \psi \rangle &= \frac{\hbar^2}{4\lambda^2} \langle (a + a^\dagger) \psi, (a + a^\dagger) \psi \rangle = \\ &= \frac{\hbar^2}{4\lambda^2} [|\alpha|^2 + \langle a^\dagger \psi, a^\dagger \psi \rangle + \alpha^2 + \bar{\alpha}^2] = \\ &= \frac{\hbar^2}{4\lambda^2} [|\alpha|^2 + |\alpha|^2 + 1 + \alpha^2 + \bar{\alpha}^2] = \\ &= \frac{\hbar^2}{4\lambda^2} [2|\alpha|^2 + 1 + \alpha^2 + \bar{\alpha}^2] \end{aligned} \quad (107)$$

Hence

$$\Delta p^2 = \frac{\hbar^2}{4\lambda^2} [2|\alpha|^2 + 1 + \alpha^2 + \bar{\alpha}^2 - \alpha^2 - \bar{\alpha}^2 - 2|\alpha|^2] = \frac{\hbar^2}{4\lambda^2} \quad (108)$$

We verified that the state is indeed a state of minimal indeterminacy

$$\Delta x \Delta p = \frac{\hbar}{2} \quad (109)$$

c)

$$\begin{aligned} a \tilde{\psi} &= \sum_{n=1}^{\infty} \frac{\alpha^n}{\sqrt{n!}} \sqrt{n} |n-1\rangle = \sum_{n=0}^{\infty} \frac{\alpha^{n+1}}{\sqrt{(n+1)!}} \sqrt{n+1} |n\rangle = \\ &= \alpha \sum_{n=0}^{\infty} \frac{\alpha^n}{\sqrt{n!}} |n\rangle = \alpha \tilde{\psi} \end{aligned} \quad (110)$$

d)

$$\langle \tilde{\psi}, \tilde{\psi} \rangle = \sum_{n=0}^{\infty} \frac{\bar{\alpha}^n}{\sqrt{n!}} \frac{\alpha^n}{\sqrt{n!}} = \sum_{n=0}^{\infty} \frac{|\alpha|^{2n}}{n!} = e^{|\alpha|^2} \quad (111)$$

Problem 2

$P(x, y, z)$ is homogenous of degree 3 and harmonic

$$\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) x y z = 0 \quad (112)$$

We have

$$\begin{aligned} H_{3,\pm 3} &= x_{\pm}^3 & H_{3,\pm 2} &= x_{\pm}^2 z \\ H_{3,1} &= x_+ z^2 - \frac{1}{4} x_+^2 x_- & H_{3,-1} &= x_- z^2 - \frac{1}{4} x_-^2 x_+ \\ H_{3,0} &= z^3 - \frac{3}{2} x_+ x_- z \end{aligned} \quad (113)$$

Hence

$$P(x, y, z) = \frac{(x_+^2 - x_-^2)}{4i} z = \frac{H_{3,2} - H_{3,-2}}{4i} \quad (114)$$

Quantum Mechanics: SERP-CHEM
Final written test: 8/1/2016

Problem 1

A particle of spin $1/2$ is subject to a uniform magnetic field which has components both along the y direction and the z direction: the interaction with the magnetic field is described by

$$\hat{H} = -\mu B_y \hat{s}_y - \mu B_z \hat{s}_z$$

with $\mu > 0$. Suppose that at the time $t = 0$ the particle is in the state with definite value $+\frac{\hbar}{2}$ of \hat{s}_z .

- a) What is the probability that at the time $t = 0$ the measurement of \hat{s}_x gives the value $+\frac{\hbar}{2}$? (Points 10%)
- b) What are the energy eigenvalues and the normalized energy eigenvectors in terms of the eigenvectors $|\pm\rangle$ of \hat{s}_z ? (Points 40 %)
- c) What is the probability that at the time $t > 0$ the particle be in the lowest energy state? Suppose $B_y = \sqrt{3} B_z$, give the numerical value for this probability. (Points 20%)
- d) What is the probability that at the time $t > 0$ the measurement of \hat{s}_z gives the value $+\frac{\hbar}{2}$? (Points 40 %)

Problem 1

- a) The state with $s_x = \frac{\hbar}{2}$ is

$$|s_x = +\rangle = \frac{1}{\sqrt{2}} (|+\rangle + |-\rangle)$$

The probability that at the time $t = 0$ the measurement of \hat{s}_x gives the value $+\frac{\hbar}{2}$ is therefore

$$P(s_x = \frac{\hbar}{2}) = |\langle s_x = + | + \rangle|^2 = \frac{1}{2}$$

- b) The energy eigenvalues are determined by the equation

$$\det \begin{pmatrix} -\frac{\hbar}{2} \mu B_z - E & i\frac{\hbar}{2} \mu B_y \\ -i\frac{\hbar}{2} \mu B_y & \frac{\hbar}{2} \mu B_z - E \end{pmatrix} = E^2 - \frac{\hbar^2}{4} \mu^2 (B_z^2 + B_y^2) = 0$$

that is

$$E_{\pm} = \pm \frac{\hbar}{2} \mu \sqrt{B_z^2 + B_y^2} \equiv \pm \frac{\hbar}{2} \mu |\vec{B}|$$

The corresponding eigenstates are

$$\psi_{\pm} = x_{\pm} |+\rangle + y_{\pm} |-\rangle$$

where

$$i B_y y_{\pm} = \left(\frac{E_{\pm}}{\frac{\hbar}{2} \mu} + B_z \right) x_{\pm} = (\pm |\vec{B}| + B_z) x_{\pm}$$

For normalized eigenvectors we must take

$$|x_{\pm}|^2 + |y_{\pm}|^2 = 1$$

$$y_{\pm} = N_{\pm} (\pm |\vec{B}| + B_z) \quad x_{\pm} = N_{\pm} i B_y$$

$$\frac{1}{N_{\pm}^2} = (B_z \pm |\vec{B}|)^2 + B_y^2 = 2 |\vec{B}| (|\vec{B}| \pm B_z)$$

$$N_{\pm}^2 = \frac{|\vec{B}| \mp B_z}{2 |\vec{B}| B_y^2}$$

$$x_{\pm} = i \sqrt{\frac{|\vec{B}| \mp B_z}{2 |\vec{B}|}} \quad y_{\pm} = \pm \sqrt{\frac{|\vec{B}| \pm B_z}{2 |\vec{B}|}}$$

with N_{\pm} real. At the time $t = 0$ the system is in the state $|+\rangle$, whose decomposition in terms of energy eigenstates is

$$\begin{aligned}\psi(0) &= |+\rangle = \psi_+ \langle\psi_+|+\rangle + \psi_- \langle\psi_-|+\rangle = \\ &= \psi_+ x_+^* + \psi_- x_-^*\end{aligned}$$

At the time t the system is in the state

$$\begin{aligned}\psi(t) &= \psi_+ x_+^* e^{-i \frac{\hbar}{2} \frac{\mu |\bar{B}|}{\hbar} t} + \psi_- x_-^* e^{i \frac{\hbar}{2} \frac{\mu |\bar{B}|}{\hbar} t} = \\ &= (x_+ |+\rangle + y_+ |-\rangle) x_+^* e^{-i \frac{\mu |\bar{B}|}{2} t} + \\ &+ (x_- |+\rangle + y_- |-\rangle) x_-^* e^{i \frac{\mu |\bar{B}|}{2} t} = \\ &= (|x_+|^2 e^{-i \frac{\mu |\bar{B}|}{2} t} + |x_-|^2 e^{i \frac{\mu |\bar{B}|}{2} t}) |+\rangle + (y_+ x_+^* e^{-i \frac{\mu |\bar{B}|}{2} t} + \\ &+ y_- x_-^* e^{i \frac{\mu |\bar{B}|}{2} t}) |-\rangle\end{aligned}$$

- c) The probability that at the time $t > 0$ the particle be in the lowest energy state is

$$\begin{aligned}P_{\psi_-}(t) &= |\langle\psi_-|\psi(t)\rangle|^2 = |x_-^* e^{-i \frac{\mu |\bar{B}|}{2} t}|^2 = |x_-^*|^2 = N_-^2 B_y^2 = \\ &= \frac{1}{2} \left(1 + \frac{B_z}{|\bar{B}|}\right)\end{aligned}$$

For $B_y = \sqrt{3} B_z$ we have

$$P_{\psi_-}(t) = \frac{1}{2} \left(1 + \frac{1}{2}\right) = \frac{3}{4}$$

- d) The probability *amplitude* that at the time t the measurement of \hat{s}_z gives the value $+\frac{\hbar}{2}$ is

$$\begin{aligned}\langle+|\psi(t)\rangle &= \langle+|\psi_+\rangle x_+^* e^{-i \frac{\mu |\bar{B}|}{2} t} + \langle+|\psi_-\rangle x_-^* e^{i \frac{\mu |\bar{B}|}{2} t} = \\ &= |x_+|^2 e^{-i \frac{\mu |\bar{B}|}{2} t} + |x_-|^2 e^{i \frac{\mu |\bar{B}|}{2} t}\end{aligned}$$

The corresponding probability is

$$\begin{aligned}
P_+(t) &= (|x_+|^2 e^{-i \frac{\mu |\vec{B}|}{2} t} + |x_-|^2 e^{i \frac{\mu |\vec{B}|}{2} t}) (|x_+|^2 e^{i \frac{\mu |\vec{B}|}{2} t} + \\
&\quad + |x_-|^2 e^{-i \frac{\mu |\vec{B}|}{2} t}) = \\
&= |x_+|^4 + |x_-|^4 + 2 |x_+|^2 |x_-|^2 \cos \mu |\vec{B}| t = \\
&= B_y^4 (N_+^4 + N_-^4 + 2 N_+^2 N_-^2 \frac{\mu |\vec{B}| t}{\hbar}) = \\
&= \frac{1}{4 |\vec{B}|^2} ((|\vec{B}| - B_z)^2 + (|\vec{B}| + B_z)^2 + 2 B_y^2 \cos \mu |\vec{B}| t) = \\
&= \frac{1}{2 |\vec{B}|^2} (|\vec{B}|^2 + B_z^2 + B_y^2 \cos \mu |\vec{B}| t) = \\
&= 1 - \frac{B_y^2}{2 |\vec{B}|^2} (1 - \cos \mu |\vec{B}| t) = 1 - \frac{B_y^2}{|\vec{B}|^2} \sin^2 \frac{\mu |\vec{B}| t}{2}
\end{aligned}$$

Quantum Mechanics: SERP-CHEM
Final written test: 1/2/2016

Problem 1

An electron moves freely in a 1-dimensional box of length $L = 10^{-10}m$. At the time $t = 0$ the particle is in the state described by the wave-function

$$\psi_0(x) = \sin \frac{\pi x}{L} + \frac{\sqrt{2}}{3} i \sin \frac{4\pi x}{L}$$

- a) What is the average energy in electronvolts of the particle at the time $t = 0$? What is the average energy at the time $t > 0$? (Points 20%)
- b) What is the average of \hat{x} at the time $t = 0$? What is the average of \hat{x} at the time $t > 0$? (Points 30 %)
- c) Compute the probability that at the time $t > 0$ the system be in the state $\psi_f(x) = \sin \frac{\pi x}{L} - \sin \frac{4\pi x}{L}$. (Points 20%)

Problem 2

The space of states for electron in a diatomic molecule is a 2-dimensional vector space with the orthonormal basis $\{|1\rangle, |2\rangle\}$ where $|1\rangle$ ($|2\rangle$) are the states in which the electron is attached to the first (second) molecule. The energy levels of the electron are described by the hamiltonian

$$H = \begin{pmatrix} E_0 & c \\ c & E_1 \end{pmatrix}$$

where c is a real parameter and $E_1 - E_0 = \Delta E > 0$. Suppose $\Delta E = 1eV$ and $c = 0.67eV$. (Points 40%)

- a) What is the probability that the electron in the ground state is attached to the first molecule?

Problem 1

- a) What is the average energy of the particle at the time $t = 0$? What is the average energy at the time $t > 0$?

The normalized wave function at the time $t = 0$ is

$$\hat{\psi}_0 = \frac{3}{\sqrt{11}} \left(\psi_1 + \frac{\sqrt{2}}{3} i \psi_4 \right) \quad (115)$$

where $\psi_n = \sqrt{\frac{2}{L}} \sin \frac{n\pi}{L}$ are the normalized energy eigenfunctions. Hence

$$\begin{aligned} \langle H \rangle &= \frac{\hbar^2 \pi^2}{2 m L^2} \left(\frac{9}{11} + 16 \frac{2}{11} \right) = \frac{\hbar^2 \pi^2}{2 m L^2} \frac{41}{11} = \\ &= \frac{41}{11} 13.6 \text{ eV} \frac{a_{Bohr}^2}{L^2} = 14.24 \text{ eV} \end{aligned} \quad (116)$$

which does not depend on time.

- b) At time $t = 0$:

$$\begin{aligned} \langle \hat{x} \rangle &= \langle \hat{\psi}_0, \hat{x} \hat{\psi}_0 \rangle = \frac{9}{11} \langle \psi_1, \hat{x} \psi_1 \rangle + \frac{2}{11} \langle \psi_4, \hat{x} \psi_4 \rangle + \\ &\quad + \frac{3\sqrt{2}i}{11} (\langle \psi_1, \hat{x} \psi_4 \rangle - \langle \psi_4, \hat{x} \psi_1 \rangle) = \\ &= \frac{9}{11} \frac{L}{2} + \frac{2}{11} \frac{L}{2} + \\ &\quad + \frac{3\sqrt{2}i}{11} (\langle \psi_1, \hat{x} \psi_4 \rangle - \langle \psi_4, \hat{x} \psi_1 \rangle) = \frac{L}{2} \end{aligned} \quad (117)$$

Putting $\Delta E = E_4 - E_1 = \frac{15\hbar^2\pi^2}{2mL^2}$, we have at time $t > 0$

$$\begin{aligned}
\langle \hat{x}(t) \rangle &= \langle \hat{\psi}_0(t), \hat{x} \hat{\psi}_0(t) \rangle = \frac{9}{11} \langle \psi_1, \hat{x} \psi_1 \rangle + \frac{2}{11} \langle \psi_4, \hat{x} \psi_4 \rangle + \\
&+ \frac{3\sqrt{2}i}{11} \left(e^{-i\frac{\Delta E t}{\hbar}} \langle \psi_1, \hat{x} \psi_4 \rangle - e^{i\frac{\Delta E t}{\hbar}} \langle \psi_4, \hat{x} \psi_1 \rangle \right) = \\
&= \frac{9}{11} \frac{L}{2} + \frac{2}{11} \frac{L}{2} + \\
&+ \frac{3\sqrt{2}i}{11} \frac{(-32)L}{225\pi^2} \left(e^{-i\frac{\Delta E t}{\hbar}} - e^{i\frac{\Delta E t}{\hbar}} \right) = \\
&= \frac{L}{2} - \frac{\sqrt{2}64L}{825\pi^2} \sin \frac{\Delta E t}{\hbar}
\end{aligned} \tag{118}$$

- c)

The norm of ψ_f is

$$\langle \psi_f, \psi_f \rangle = \frac{L}{2} + \frac{L}{2} = L \tag{119}$$

and the normalized final state is

$$\hat{\psi}_f(x) = \frac{1}{\sqrt{2}} (\psi_1(x) - \psi_4(x)) \tag{120}$$

The transition amplitude is

$$\langle \hat{\psi}_f, \hat{\psi}_0(t) \rangle = \frac{1}{\sqrt{2}} \frac{3}{\sqrt{11}} e^{-i\frac{E_1 t}{\hbar}} - \frac{1}{\sqrt{2}} \frac{\sqrt{2}}{\sqrt{11}} i e^{-i\frac{E_4 t}{\hbar}} \tag{121}$$

and the probability amplitude is

$$\begin{aligned}
P_{i \rightarrow f}(t) &= \frac{9}{2 \times 11} + \frac{1}{11} - \frac{6}{11\sqrt{2}} \sin \frac{\Delta E t}{\hbar} = \\
&= \frac{1}{2} - \frac{6}{11\sqrt{2}} \sin \frac{\Delta E t}{\hbar}
\end{aligned} \tag{122}$$

Problem 2

- a)

The energy levels of the electron are

$$E_{\pm} = E_0 + \frac{\Delta E \pm \sqrt{\Delta E^2 + 4c^2}}{2} \quad (123)$$

The corresponding eigenstates are

$$|E_{\pm}\rangle = x_{\pm}|1\rangle + y_{\pm}|2\rangle \quad (124)$$

where

$$(E_{\pm} - E_0)x_{\pm} = cy_{\pm} \quad (125)$$

The (not normalized) ground state is

$$|E_{-}\rangle = |1\rangle + \frac{\Delta E - \sqrt{\Delta E^2 + 4c^2}}{2c} |2\rangle \quad (126)$$

The probability for an electron in the ground state to be attached to the first atom is

$$\begin{aligned} P_1 &= \frac{|\langle 1|E_{-}\rangle|^2}{\langle E_{-}|E_{-}\rangle} = \frac{1}{1 + \frac{(\Delta E - \sqrt{\Delta E^2 + 4c^2})^2}{4c^2}} = \\ &= \frac{4x^2}{4x^2 + (1 - \sqrt{1 + 4x^2})^2} \end{aligned} \quad (127)$$

where

$$x = \frac{c}{\Delta E} \quad (128)$$

For

$$x = 0.67 \quad (129)$$

$$P_1 = 0.80 \quad (130)$$