Chem 120A Midterm 2

Justin Yeung

TOTAL POINTS

23 / 30

QUESTION 1

1 Question 1 2 / 2

✓ **+ 2 pts** -i or 1/i

+ 1 pts Correct start, mathematical error

+ 0 pts Incorrect

QUESTION 2

2 Question 2 2 / 2

✓ **+ 1 pts** Not Hermitian (with fully correct assumptions). Could only receive this in conjunction with item 2.

✓ **+ 1 pts** Because a^dagger not equal to a (or statement of the relation)

+ 0 pts Incorrect assumption (commute = Hermitian) leading to statement of non-Hermitian. Commuting is a consequence of self-adjointness, not a cause.

+ 0 pts Incorrect assumption leading to statement of non-Hermitian

+ 0 pts Incorrect

+ 0 pts Commute = Hermitian

QUESTION 3

3 Question 3 2 / 2

✓ **+ 1 pts** a^dagger a | psi> = w | psi>

✓ **+ 1 pts** < psi | a^dagger a | psi > = < psi' | psi' >, which must be greater than or equal to 0. Refer to class notes from 2/22. This proof is the only acceptable answer.

+ 0 pts Incorrect. Note: a^dagger a = h - 1/2. Also note that the killer condition is a byproduct of, not the cause of, this fact.

+ 1 pts Almost full proof, minor error

QUESTION 4

4 Question 4 4 / 4

✓ **+ 2 pts** If they have common eigenvectors, they must commute

✓ **+ 2 pts** Explicitly compute commutator using either a/a^dagger or r/q versions of operators

+ 4 pts Fully correct proof without commutation using h = a^dagger a + 1/2

+ 0 pts Incorrect

+ 1 pts Commutator attempt with a mistake, incomplete

+ 2 pts Statement similar to the proof for item 3, no proof. Or, attempt at proof that has a minor mistake or is incomplete.

- 1 pts Incorrect definition of h (correct: h = a^dagger a + 1/2)

QUESTION 5

5 Question 5 2 / 2

✓ **+ 1 pts** [Li,Lj] not zero. Hence, you can only know one direction

✓ **+ 1 pts** [L^2,Lj]=0. Hence you are allowed to know one component and L^2

+ 0 pts incorrect

QUESTION 6

6 Question 6 2 / 2

✓ **+ 1 pts** m=2

✓ **+ 1 pts** Hence, l must be greater equal than 2 because l=m_max

+ 0 pts incorrect

QUESTION 7

7 Question 7 0 / 2

+ 1 pts [L^2,L_] =0, they commute

+ 1 pts L^2 (L_|x>) = L_(L^2|x>)

✓ **+ 0 pts** incorrect

QUESTION 8

8 Question 8 **3 / 3**

✓ **+ 1 pts Energy levels are 0 2 6 and 12 for J = 0, 1, 2, 3**

✓ **+ 1 pts ΔJ= +/-1 bc it has a permanent dipole moment**

✓ **+ 1 pts Show allowed transition in the sketch.**

+ **0 pts** Click here to replace this description.

QUESTION 9

9 Question 9 **2 / 2**

✓ **+ 1 pts E^(0)_0=H[1,1]= -1**

✓ **+ 1 pts E^(1)_0=V[1,1]=1**

+ **0 pts** incorrect.

+ **0 pts** No bonus point was given for this question

QUESTION 10

10 Question 10 **1 / 3**

✓ **+ 1 pts Only the third excited state couples with the 1st excited state (V[4,2]=1, others are 0)**

+ **1 pts** c_(41)= -V41/(E_4 - E_1)

+ **1 pts** c_(41)= -1/7

+ **0 pts** incorrect.

QUESTION 11

11 Question 11 **1 / 2**

+ **1 pts** If there are degenerate states / |c_ij| is large

+ **1 pts** applies here as E^(0)_2=E^(0)_3 hence |c_23 | is not well defined

✓ **+ 1 pts Perturbation needs be small/ mutually exclusive to 1**

+ **0 pts** incorrect.

QUESTION 12

12 Question 12 **2 / 4**

+ **1 pts** Choose states 2 and 3 because the energies of 1 and 4 are too low/high

✓ **+ 1 pts Set up the H-Matrix**

✓ **+ 1 pts solve for the eigenvalues**

+ **1 pts** Pick the right eigenvalue

+ **0 pts** incorrect.

Chemistry 120A

Spring Semester, 2019; Prof. Head-Gordon
2nd Mid-Term Exam: Thursday March 21

Name: Justin Yeung

Instructions: (1) Keep calm, write clearly so we can give partial credit! Do all questions.
(2) The exam is closed book.
(3) The exam has 6 pages (use blank back sides as scratch paper (not graded).

Grade:

Problem 1: Harmonic oscillator (10 points) ________________

Problem 2: Angular momentum (9 points) ________________

Problem 3: Approximation methods (11 points) ________________

Total (30 points) ________________

Useful facts and figures:

h=6.626755×10^{-34} J s

k=1.380658×10^{-23} J K^{-1}

N_A=6.022137×10^{23} mol^{-1}

1 eV = 1.60219×10^{-19} J

$\hbar = h/(2\pi)$

$$ax^2 + bx + c = 0$$
$$\Rightarrow x = \left(-b \pm \sqrt{b^2 - 4ac}\right)\big/2a$$

$$\hat{H} = \frac{\hat{p}^2}{2m} + V(x)$$

$$\hat{p} = \frac{\hbar}{i}\frac{\partial}{\partial x}$$

$$\hat{H}|\psi\rangle = \frac{-\hbar}{i}\frac{\partial}{\partial t}|\psi\rangle$$

$$\Delta p \Delta x \geq \hbar/2$$

$$\left[\hat{A},\hat{B}\right] = \hat{A}\hat{B} - \hat{B}\hat{A}$$

Justin Y.

Question I. The harmonic oscillator problem involves the dimensionless Hamiltonian:

$$\hat{h} = \frac{1}{2}\hat{r}^2 + \frac{1}{2}\hat{q}^2$$

Here a dimensionless position is q, and a dimensionless momentum is $\hat{r} = \frac{1}{i}\frac{d}{dq}$.

1. (2 points) Evaluate the commutator $[\hat{r},\hat{q}]$. Show all working for full credit.

$[\hat{r},\hat{q}]f = \hat{r}\hat{q}f - \hat{q}\hat{r}f$ f = dummy function in terms of q

$= \frac{1}{i}\frac{d}{dq}qf - q\frac{1}{i}\frac{d}{dq}f$

$= \frac{1}{i}\left(f + q\frac{df}{dq}\right) - q\frac{1}{i}\frac{df}{dq}$

$= \frac{1}{i}f + \cancel{\frac{q}{i}\frac{df}{dq}} - \cancel{\frac{q}{i}\frac{df}{dq}}$

$\hat{h} = \hat{a}\hat{a} + \frac{1}{2}$

$[\hat{r},\hat{q}]\cancel{f} = \frac{1}{i}\cancel{f}$

$\boxed{[\hat{r},\hat{q}] = \frac{1}{i} = -i}$

2. (2 points) An operator is defined as $\hat{a} = \frac{1}{\sqrt{2}}(\hat{q} + i\hat{r})$. Show whether or not it is Hermitian.

Hermitian if $\hat{a} = \hat{a}^+$

$\hat{a}^+ = \frac{1}{\sqrt{2}}(\hat{q} - i\hat{r})$

$\sqrt{2}\,\hat{a}$

$\boxed{\text{Since } \hat{a}^+ \neq \hat{a},\ \hat{a} \text{ is not hermitian}}$

3. (2 points) Show that the eigenvalues of $\hat{a}^\dagger\hat{a}$ cannot be negative.

say l is some eigenvalue of $\hat{a}^+\hat{a}$ on normalized eigenfunction $|lm\rangle$

$\hat{a}^+\hat{a}|lm\rangle = \omega|lm\rangle$

$\langle lm|\hat{a}^+\hat{a}|lm\rangle = \langle lm|\omega|lm\rangle$ project with $\langle lm|$

$\langle lm|\omega|lm\rangle = \langle\hat{a}\,lm|\hat{a}\,lm\rangle$

$\omega = \langle\hat{a}\,lm|\hat{a}\,lm\rangle \geq 0$

Scalar multiplication ≥ 0 if two items are the same

Justin Y.

4. (4 points) Suppose we have an eigenvector of $\hat{a}^{\dagger}\hat{a}$. Show that it is also an eigenvector of $\hat{h}$.

$[\hat{a}^{+}\hat{a}, \hat{h}] = 0$ · if have common eigenvectors, then $\hat{a}^{+}\hat{a}$ and $\hat{h}$ will commute

$\hat{a}^{+}\hat{a} = \frac{1}{\sqrt{2}}(\hat{q} - i\hat{r})\frac{1}{\sqrt{2}}(\hat{q} + i\hat{r}) = \frac{1}{2}(\hat{q}\hat{q} + i\hat{q}\hat{r} - i\hat{r}\hat{q} + \hat{r}\hat{r})$
$= \frac{1}{2}(\hat{q}^2 + i\hat{q}\hat{r} - i\hat{r}\hat{q} + \hat{r}^2)$

$[\hat{a}^{+}\hat{a}, \hat{h}] = \hat{a}^{+}\hat{a}\hat{h} - \hat{h}\hat{a}^{+}\hat{a}$

$= \frac{1}{2}(\hat{q}^2 + i\hat{q}\hat{r} - i\hat{r}\hat{q} + \hat{r}^2)\frac{1}{2}(\hat{r}^2 + \hat{q}^2) - \frac{1}{2}(\hat{r}^2 + \hat{q}^2)\frac{1}{2}(\hat{q}^2 + i\hat{q}\hat{r} - i\hat{r}\hat{q} + \hat{r}^2)$

$= \frac{1}{4}(\cancel{\hat{q}^2\hat{r}^2} + \cancel{\hat{q}^4} + i\hat{q}\hat{r}^3 + i\hat{q}\hat{r}\hat{q}^2 - i\hat{r}\hat{q}\hat{r}^2 - i\hat{r}\hat{q}^3 + \cancel{\hat{r}^4} + \cancel{\hat{r}^2\hat{q}^2} - \cancel{\hat{r}^2\hat{q}^2} - i\hat{r}^2\hat{q}\hat{r}$
$+ i\hat{r}^2\hat{r}\hat{q} - \cancel{\hat{r}^4} - \cancel{\hat{q}^4} - i\hat{q}^3\hat{r} + i\hat{q}^2\hat{r}\hat{q} - \cancel{\hat{q}^2\hat{r}^2})$

$= \frac{i}{4}(\hat{q}\hat{r}^3 + \hat{q}\hat{r}\hat{q}^2 - \hat{r}\hat{q}\hat{r}^2 - \hat{r}\hat{q}^3 - \hat{r}^2\hat{q}\hat{r} + \hat{r}^3\hat{q} - \hat{q}^3\hat{r} + \hat{q}^2\hat{r}\hat{q})$

$\hat{a} = \frac{1}{\sqrt{2}}(\hat{q} + i\hat{r})$
$\sqrt{2}\hat{a} = \hat{q} + i\hat{r}$
$\hat{q} = \sqrt{2}\hat{a} - i\hat{r}$

$\hat{a}^{+} = \frac{1}{\sqrt{2}}(\hat{q} - i\hat{r})$
$= \frac{1}{\sqrt{2}}(\sqrt{2}\hat{a} - i\hat{r} - i\hat{r})$
$\hat{a}^{+} = \hat{a} - \frac{2i}{\sqrt{2}}\hat{r}$
$\hat{a}^{+} = \hat{a} - \sqrt{2}i\hat{r}$
$\hat{r} = (\hat{a} - \hat{a}^{+})\frac{-i}{\sqrt{2}}$
$\hat{r} = \frac{i}{\sqrt{2}}(\hat{a}^{+} - \hat{a})$

$\hat{q} = \sqrt{2}\hat{a} - i(\frac{i}{\sqrt{2}}(\hat{a}^{+} - \hat{a}))$
$= \sqrt{2}\hat{a} + \frac{1}{\sqrt{2}}\hat{a}^{+} - \frac{1}{\sqrt{2}}\hat{a}$
$\hat{q} = \frac{1}{\sqrt{2}}(\hat{a}^{+} + \hat{a})$
$\hat{h} = \frac{1}{2}\hat{q}^2 + \frac{1}{2}\hat{r}^2$
$= \frac{1}{2}(\frac{1}{2}(\hat{a}^{+}\hat{a}\quad)$
$= (\hat{a}\hat{a}^{+} + \hat{a}\hat{a}^{+})\frac{1}{2}$

$[\hat{a}^{+}\hat{a}, h]$
$= [\hat{a}^{+}\hat{a}, (\hat{a}\hat{a}^{+} + \hat{a}\hat{a})\frac{1}{2}]$
$= \hat{a}^{+}\hat{a}\hat{a}\hat{a}^{+} + \hat{a}^{+}\hat{a}\hat{a}^{+}\hat{a}$
$- \hat{a}^{+}\hat{a}\hat{a}\hat{a}^{+} - \hat{a}^{+}\hat{a}\hat{a}\hat{a}$
$= \boxed{0}$

Question II. Classically, the angular momentum vector is defined as the cross product of the position vector **r** and the momentum vector **p**, $\mathbf{L} = \mathbf{r} \times \mathbf{p}$, which then leads to the quantum operator: $\hat{\mathbf{L}} = \hat{\mathbf{r}} \times \hat{\mathbf{p}}$. The components of $\hat{\mathbf{L}}$ do not commute; for example: $[\hat{L}_x, \hat{L}_y] = i\hbar\hat{L}_z$, etc. However the components do commute with total angular momentum, $\hat{L}^2 = \hat{\mathbf{L}} \cdot \hat{\mathbf{L}}$, so that $[\hat{L}^2, \hat{L}_j] = 0$ for $j=x,y,z$.

5. (2 points) Use the commutation relations to show what information can be known about angular momentum in a given eigenstate of rotational motion, $|\chi\rangle$.

$[\hat{L}^2, \hat{L}_j] = 0$ for $j = x, y, z$

↳ we can know both total angular momentum and only one of the components in a given eigenstate $|x\rangle$

$\left\{ \begin{array}{l} \hat{L}^2|x\rangle = \hbar^2 l(l+1)|x\rangle \\ L_j|x\rangle = m|x\rangle \quad \text{for } j = x, y, z \end{array} \right\}$

Justin Y.

6. (2 points) If it is known that $\hat{L}_z|\chi\rangle = 2\hbar|\chi\rangle$ then explain (with logic) what eigenvalues of $\hat{L}^2 = \hat{\mathbf{L}} \bullet \hat{\mathbf{L}}$ are *not* possible for the state $|\chi\rangle$. (Note that if $|\chi\rangle$ is an eigenstate of $\hat{L}^2$ then its eigenvalues are $\hat{L}^2|\chi\rangle = \hbar^2 l(l+1)|\chi\rangle$ where l is zero or a positive integer).

If $\hat{L}_z|x\rangle = 2\hbar|x\rangle$, then we know the angular momentum eigenvalue via the z-axis is 2, which is the m value. The m value takes form of $m = l, l-1, l-2 \ldots -l$. Thus $l = 2, 3, 4, 5 \ldots$. Thus, eigenvalues of $l = 1$ or 0 are possible. From logic, $L^2 >> \hat{L}_z$ since it is the sum of all of its components squared (which cant be negative), so the total angular momentum eigenvalue always greater than that of component.

7. (2 points) If we form an angular momentum destruction operator as $\hat{L}_- = \hat{L}_x - \hat{L}_y$, then show whether or not $\hat{L}_-|\chi\rangle$ has the same eigenvalue of $\hat{L}^2$ as $|\chi\rangle$ itself.

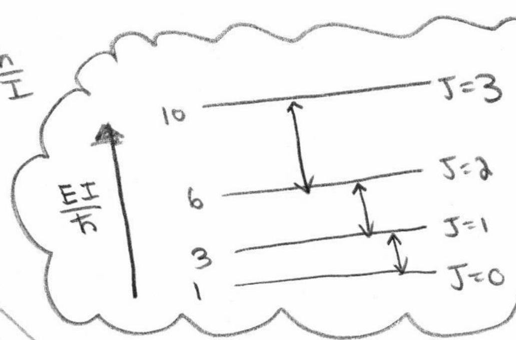
$$\hat{L}_-|x\rangle = (\hat{L}_x - \hat{L}_y)|x\rangle = \hat{L}_x|x\rangle - \hat{L}_y|x\rangle$$
$$= \hbar\omega_1|x\rangle - \hbar\omega_2|x\rangle = \hbar\omega_T|x\rangle$$
$$\hat{L}^2(\hat{L}_-|x\rangle) = [\hbar^2(l)(l+1)]\hbar\omega_T|x\rangle$$

Same eigenvalue since L^2's eigenvalues do not mix w/ $\hat{L}_-$ eigenvalues, so L^2's values are not affecting.

8. (3 points) The HCl molecule's rotational energy is described by the Hamiltonian, $\hat{H} = \frac{1}{2}\hat{L}^2/I$ where I is the moment of inertia of the molecule. Sketch the energy level diagram including the first 4 levels, and show what transitions are allowed, if any.

$E = \frac{\hbar}{2I} J(J+1)$ for linear molecules

$$E_1 = \frac{\hbar}{2I}(1+1)(1) = \frac{\hbar}{2I}(2) = \frac{\hbar}{I}$$
$$E_2 = \frac{\hbar}{2I}(2)(2+1) = \frac{\hbar}{2I}(6) = 3\frac{\hbar}{I}$$
$$E_3 = \frac{\hbar}{2I}(3)(3+1) = \frac{\hbar}{2I}(12) = 6\frac{\hbar}{I}$$
$$E_4 = \frac{\hbar}{2I}(4)(4+1) = \frac{\hbar}{2I}(20) = 10\frac{\hbar}{I}$$



Because of the selection rule, only transitions of $\Delta J = \pm 1$ are allowed.

Justin Y.

Question III. Approximation methods. Let us consider a 4-level system, with an unperturbed Hamiltonian $\hat{H}^{(0)}$, subject to a perturbation $\hat{H}^{(1)} = \lambda\hat{V}^{(1)}$. In the basis of unperturbed eigenstates (let's label them by their row and column position 1,2,3,4):

$$\mathbf{H}^{(0)} = \begin{bmatrix} -1 & 0 & 0 & 0 \\ 0 & 3 & 0 & 0 \\ 0 & 0 & 3 & 0 \\ 0 & 0 & 0 & 6 \end{bmatrix}; \qquad \lambda\mathbf{V}^{(1)} = \frac{1}{2}\begin{bmatrix} 1 & 0 & 0 & 1 \\ 0 & 0 & 1 & 1 \\ 0 & 1 & 0 & 1 \\ 1 & 1 & 1 & -1 \end{bmatrix}$$

9. (2 points) Given that perturbation theory for the energy of the jth state is: $E_j = E_j^{(0)} + \lambda E_j^{(1)} + \lambda^2 E_j^{(2)} + \ldots$ and $E_j^{(1)} = \langle \Psi_j^{(0)} | \hat{V}^{(1)} | \Psi_j^{(0)} \rangle$, obtain the zero order energy and the first order correction for the ground state of the 4-level system above.

ground state $\psi = \begin{bmatrix}1\\0\\0\\0\end{bmatrix}$

$E_0^{(0)} = \langle \psi_0^{(0)} | H^{(0)} | \psi_0^{(0)} \rangle = H_{00}^{(0)} = \boxed{-1 \text{ for zero order E @ ground state}}$

$E_0^{(1)} = \langle \psi_0^{(0)} | V^{(1)} | \psi_0^{(0)} \rangle = V_{00}^{(1)} = 1$

$\rightarrow$ total first order correction $= \lambda E_0^{(1)} = \frac{1}{2}(1) = \boxed{\frac{1}{2}}$

10. (3 points) Which excited states have non-zero coupling with the ground state in first order perturbation theory? Evaluate any non-zero couplings, recalling that the first order perturbed wavefunction is $|\Psi_j^{(1)}\rangle = \sum_{k \neq j} |\Psi_k^{(0)}\rangle c_{kj}^{(1)}$, and $c_{kj}^{(1)} = -\langle \Psi_k^{(0)} | \hat{V}^{(1)} | \Psi_j^{(0)} \rangle / (E_k^{(0)} - E_j^{(0)})$.

$k = 0$ = ground state

① $c_{01}^{(1)} = \dfrac{-\langle \psi_0^{(0)} | \hat{V}^{(1)} | \psi_1^{(0)} \rangle}{E_0^{(0)} - E_1^{(1)}} = \dfrac{-\hat{V}_{01}}{-1-3} = \dfrac{-[1000][\hat{V}^{(1)}]\begin{bmatrix}0\\1\\0\\0\end{bmatrix}}{-4} = 0$

② $c_{02}^{(1)} = \dfrac{-\hat{V}_{02}}{-1-3} = \dfrac{-[1000][\hat{V}^{(1)}]\begin{bmatrix}0\\0\\1\\0\end{bmatrix}}{-4} = 0$

③ $c_{03}^{(1)} = \dfrac{-\hat{V}_{03}}{-1-6} = \dfrac{-[1000][\hat{V}^{(1)}]\begin{bmatrix}0\\0\\0\\1\end{bmatrix}}{-7} = \frac{1}{7}$

3rd excited state $\left(\begin{bmatrix}0\\0\\0\\1\end{bmatrix}\right)$ has non-zero coupling w/ ground state. $|\psi_3\rangle = |\psi_{(0)}^{(0)}\rangle c_{03}^{(1)}$

$|\psi_3\rangle = \frac{1}{7}\begin{bmatrix}1\\0\\0\\0\end{bmatrix}$

11. (2 points) Under what conditions does second order perturbation theory for the energy fail, in the sense that the power series might not be converging? Would such conditions apply to any states in this problem? (recall that $E_j^{(2)} = \langle \Psi_j^{(0)} | \hat{V}^{(1)} | \Psi_j^{(1)} \rangle$, with $|\Psi_j^{(1)}\rangle$ defined above)

Since $\lambda < 1$, we expect the powerseries to converge in our case, as the perturbations are λ^n or $\frac{1}{2^n}$ which ultimately converges. However, if $E_j^{(2)} = 0$, then series will not converge either.

$E_j^{(2)} = 0 = \langle \psi_j^{(0)} | V^{(1)} | \psi_j^{(1)} \rangle \Rightarrow \boxed{V_{ij} V_{ji} = 0}$ $\boxed{\text{This occurs @ ground state w/ 1st and 2nd excited states as well as 1st \& 2nd states alone.}}$

12. (4 points) Apply the linear variational method (recall that for orthonormal functions this is solving $\mathbf{HC} = \mathbf{CE}$, where $\mathbf{C}$ contains the expansion coefficients) with two trial functions to

Justin Y.

model the first excited state of the 4-level system above. State clearly which 2 states you choose to use, and why, and then evaluate the variational energy, reporting your two values.

$$\hat{H} = \hat{H}^{(0)} + \lambda \hat{V}^{(1)} = \begin{bmatrix} -\frac{1}{2} & 0 & 0 & \frac{1}{2} \\ 0 & 3 & \frac{1}{2} & \frac{1}{2} \\ 0 & \frac{1}{2} & 3 & \frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} & \frac{1}{2} & 11/2 \end{bmatrix}$$

To model the transition to the first excited state, we will pick the two trial functions to be ground and 1st excited state ($\begin{bmatrix}1\\0\\0\\0\end{bmatrix}$ and $\begin{bmatrix}0\\1\\0\\0\end{bmatrix}$) since this is what the problem wants since it's going from ground to 1st excited state. Because of this, we can simply the matrix to be its top left quadrant:

$$\hat{H} = \begin{bmatrix} -1/2 & 0 \\ 0 & 3 \end{bmatrix}$$

$$\hat{H} \underline{c} = E \underline{c}$$

$$(\hat{H} - ES)\underline{c} = 0 \qquad S = \delta_{ij} = \begin{cases} 1 & \text{if } j = i \\ 0 & \text{if } j \neq i \end{cases}$$

$$\begin{bmatrix} -1/2 - E & 0 \\ 0 & 3 - E \end{bmatrix} = 0.$$

$$(-\tfrac{1}{2} - E)(3 - E) = 0$$

$$\boxed{E = -\tfrac{1}{2} \text{ and } 3}$$