## April 7, 2009

1 hour, 30 min
Chemistry 218, Molecular Structure
First Examination- Spring 2009
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Name:

## ID number:

## Signature:

## Useful information:

Permittivity of vacuum: $\varepsilon_{0}=8.854187816 \times 10^{-12} \mathrm{C}^{2} \cdot \mathrm{~J}^{-1} . \mathrm{m}^{-1}$
$4 \pi \varepsilon_{0}=1.112650056 \times 10^{-10} \mathrm{C}^{2} \cdot \mathrm{~J}^{-1} \cdot \mathrm{~m}^{-1}$
Bohr magneton: $\beta=9.2740154 \times 10^{-24} \mathrm{~J} . \mathrm{T}^{-1}$
Planck constant: $h=6.6260755 \times 10^{-34} \mathrm{~J}$. s
Proton charge: $e=1.60217733 \times 10^{-19} \mathrm{C}$
Speed of light in vacuum: $c=2.99792458 \times 10^{8} \mathrm{~m} . \mathrm{s}^{-1}$
Electron rest mass: $m_{e}=9.1093897 \times 10^{-31} \mathrm{~kg}$
Bohr radius: $a_{0}=5.29177249 \times 10^{-11} \mathrm{~m}$
$\Psi(x)=\left(\frac{2}{L}\right)^{1 / 2} \sin \frac{n \pi x}{L}$ for a particle in a box $\quad E_{n}=\frac{n^{2} h^{2}}{8 m L^{2}}$ for a particle in a box
$\sin x \sin y=\frac{1}{2} \cos (x-y)-\frac{1}{2} \cos (x+y) \quad E_{n}=\frac{-m_{e} e^{4}}{32 \pi^{2} \varepsilon_{0}^{2} \hbar^{2} n^{2}}=\frac{-e^{2}}{8 \pi \varepsilon_{0} a_{o} n^{2}}$ or $\frac{-e^{2}}{2 a_{o} n^{2}}$ for H atom
O is hermitian: $\langle m| O|n\rangle=\langle n| O|m\rangle^{*}$
$\nabla^{2}=\frac{1}{r^{2}} \frac{\partial}{\partial r}\left(r^{2} \frac{\partial}{\partial r}\right)+\frac{1}{r^{2} \sin \theta} \frac{\partial}{\partial \theta}\left(\sin \theta \frac{\partial}{\partial \theta}\right)+\frac{1}{r^{2} \sin ^{2} \theta} \frac{\partial^{2}}{\partial \phi^{2}}$
$d \tau=r^{2} \sin \theta d r d \theta d \phi$
$\Psi_{0}(x)=\left(\frac{\alpha}{\pi}\right)^{1 / 4} e^{-\alpha x^{2} / 2} ; \Psi_{1}(x)=\left(\frac{4 \alpha^{3}}{\pi}\right)^{1 / 4} x e^{-\alpha x^{2} / 2}$ for 1D harmonic oscillator; $\alpha=\frac{(k \mu)^{1 / 2}}{\hbar}$

$$
\int^{\infty} x^{2 n} e^{-c x^{2}} d x=\frac{1.3 .5 \ldots(2 n-1)}{2^{n+1}} \sqrt{\frac{\pi}{\alpha^{2 n+1}}} \quad \int_{0}^{\infty} x^{n} e^{-a x} d x=\frac{n!}{a^{n+1}} ; \text { n is a positiveinteger }
$$

Harmonic oscillator energy: $E_{v}=\left(u+\frac{1}{2}\right) h v ; v=0,1,2,3 \ldots . \quad v=\frac{1}{2 \pi}\left(\frac{k}{\mu}\right)^{1 / 2}$
Rigid rotor energy: $E_{j}=\frac{\hbar^{2}}{2 I} J(J+1) ; J=0,1,2,3 \ldots$
Part I. $(24 \%)$ Instructions: Circle one answer. No penalty. 4 points each.

- Assuming an internuclear distance of 127.5 pm in $\mathbf{D}^{35} \mathrm{Cl}$, compute the expected line separation in $\mathrm{cm}^{-1}$ for the absorption peaks corresponding to absorption from $\quad Y=\frac{m_{1} m_{2}}{m_{1}+m_{2}}$ $\mathrm{J}=0 \rightarrow \mathrm{~J}=1$. (atomic masses: $\mathrm{D}=2.0141$ atm. $\cdot{ }^{35} \mathrm{Cl}=34.9688$ a.m.u).
a. $10.90 \mathrm{~cm}^{-1}$
c. $6.74 \mathrm{~cm}^{-1}$
$2 \widehat{B}$
d. $120.0 \mathrm{~cm}^{-1}$
$2 \tilde{B}=2 B\left(H_{2}\right)=10.90 \mathrm{~cm}^{-1}$
e. $22.40 \mathrm{~cm}^{-1} \quad 2 B=\frac{2 B(2)}{C}=210.90 \mathrm{~cm}^{-1}$
f. None of the above, the line separation 13
- The Spherical Harmonics, wavefunction solutions of the Rigid Rotor, are eigenfunction of which of the following operators:
a. $\quad \mathbf{H}$, the Hamiltonian of the H -atom
b. $\quad \mathbf{L}^{2}$, where $\mathbf{L}$ is the angular momentum operator $\longrightarrow$
c. $\quad \mathbf{L}_{2}$, the angular momentum operator along the $z$-direction
see back
$\mathbf{L}^{2} / 2 \mathrm{I}$, where $\mathbf{L}$ is the angular momentum operator, and I is the moment of inertia
All of the above
b), c), and d)
- The IR-vibrational spectrum of $\mathrm{H}^{81} \mathbf{B r}$ consists of one intense line at $2461 \mathrm{~cm}^{-1}$. The force constant of the bond between hydrogen and bromine is:
$\begin{array}{lll}\text { a. } 478 \mathrm{N.m}^{-1} & \tilde{\nu}=2461 \mathrm{~cm}^{-1} & \mathcal{H}=\frac{m_{1} m_{2}}{m_{1}+m_{2}}=\frac{89 \times 10^{-3}}{a_{0 \times 1}}=1.642 \times 10^{-27 \mathrm{~kg}}\end{array}$
c. $2912 \mathrm{~N} \mathrm{~m}^{-1} \quad v_{s^{-}}=c \tilde{\nu}=\frac{1}{2 \pi}\left(\frac{h_{k}}{\mu}\right)^{1 / 2} \Rightarrow k=\mu c^{2} \tilde{v}^{2} 4 \pi^{2}=1.642 \times 10^{-27} \mathrm{~kg} x$
c. $406 \mathrm{N.m}^{-1} \quad\left(2.9979 \times 10^{8} \mathrm{~ms}^{-1}\right) \times\left(2641 \mathrm{~cm}^{-1} \times 1 \mathrm{c}^{2} \mathrm{~cm} / \mathrm{m}\right)^{2} \times 4 \pi^{2}=406 \mathrm{Nm}^{-1}$
e. None of the above. The answer is
- Which of the following functions is an "unacceptable" wavefunction to describe a system over the indicated interval.
a. $\sin ^{-1}(x) ; x(-1,1) \rightarrow$ unacceptable, mullivalued function $\sin ^{-1} 1=\frac{\pi}{2}, \frac{\pi}{2}+2 \pi, \frac{\pi}{2}+4 \pi \ldots$
b. $\exp \left(-x^{2}\right) ; x(-\infty, \infty)$
c. $\exp (-\beta x)$, where $\beta$ is a negative real number; $x(-\infty, \infty) \rightarrow$ unacceptable, $\alpha \infty x \rightarrow \infty, e^{-\beta x} \rightarrow \infty$
d. $\exp \left(-\mathrm{r}^{2}\right) ; \mathrm{r}(0, \infty)$
(e. a) and c)
- Consider the following wavefunction, which is a solution to the Schrödinger equation for the H -atom:

$$
\Psi=\left(\frac{1}{a_{0}}\right)^{3 / 2}\left(27-\frac{18 r}{a_{0}}+\frac{2 r^{2}}{a_{0}^{2}}\right) \exp \left(-r / 3 a_{0}\right)
$$

This function corresponds to which of the following orbitals? (Hint: you should be able to do this by inspection)
2radial nodes, o angular nodes

| a. | 2 s |
| :--- | :--- |
| (b.) | 3 s |
| c. | $3 \mathrm{p}_{x}$ |
| d. | $4 \mathrm{p}_{\mathrm{y}}$ |
| c. | 4 s |

- Consider a linear polyene molecule (with $6 \pi$ electrons) of length 0.95 nm (assumed linear). Calculate the wavelength of light required to promote an electron from the $3^{\text {rd }}$ to the $4^{\text {th }}$ energy level.
a. $\quad 495 \mathrm{~nm} \quad \Delta E=\frac{h L}{\lambda}=\frac{h^{2}}{8 \mathrm{~mL}^{2}}(16.9) \Rightarrow \lambda=\frac{8 \mathrm{~mL}^{2} \mathrm{c}}{h(16.9)}=\frac{8 \times 9.1093879 \times 10^{-3} \mathrm{Kg}}{6.6265755 \times 10^{-34} \mathrm{~J} \cdot \mathrm{~s}} \times$
$\begin{array}{ll}\text { b. } & 460 \mathrm{~nm} \\ \text { c. } & 595 \mathrm{~nm} \\ \left(0.95 \times 10^{-9} \mathrm{~m}\right)^{2} \times 2.9979 \times 10^{8} \mathrm{~ms}^{-1} & =4.25 \times 10^{-7} \mathrm{~m}=425 \mathrm{~nm}, ~\end{array}$
(d.) $425 \mathrm{~nm}(16-9)$
e. None of the above. The answer is

Part II. (20\%) Instructions: Circle T for True or F for False, $\mathbf{2}$ points each, no penalty.

If a wavefunction $\Psi$ is a linear combination of several eigenfunction $\left(\Phi_{n}\right)$ of the operator $\hat{A}$ (corresponding to an observable A ) then each measurement of the property A for a system in a state described by this wavefunction $\Psi$ will be an eigenvalue of an eigenfunction $\left(\Phi_{n}\right)$ in the linear combination. T F

The zero point energy for a harmonic oscillator is zero.
T


Microscopic particles that are confined in space exhibit quantization of their eigenspectrum (quantization of energy levels) T F

If a system is in a state described by the wavefunction $\psi$, which is an eigenfunction of operator $\hat{A}$ then a measurement on the system in this state of the observable A can give any value as long as the average of all measurements is the eigenvalue a $(\hat{A} \psi=a \psi)$

The spacing of the electronic energy levees under the potential energy of the H -atom decreases with increasing principal quantum number $n$, while the energy spacing for a quantum mechanical harmonic oscillator increases as the quantum number $v$ increases.

T
(F)

A particle according to quantum mechanics can exist in a region where its kinetic energy would be negative, whereas classically the particle cannot be present in such a region.

An increase in particle mass would decrease the ground state energy of both a quantum particle-in-a-box and a quantum harmonic oscillator.
(I) F

The Gross selection rule for a molecule to have a rotational absorption spectrum is that the molecule has a permanent dipole moment.

A free microscopic particle confined in space must have a non-zero (finite) zero-point energy, otherwise the system will be in defiance of the Heisenberg Uncertainty principle.
(T) F

The kinetic energy and the potential energy for an electron in an H-atom orbital can be determined simultaneously to arbitrarily high precision since each orbital wavefunction is an eigenfunction of the Hamiltonian operator, and therefore the electron in that orbital has a constant total encegy (the eigenvalue). T (F)

## Part III. (56 \%)

III. 1 ( $6 \%$ ) For each of the following operators indicate by "yes" or "no" whether $\Psi_{\left(2 P_{y}\right)}$ (with $\mathrm{z}=1 ; \mathrm{H}$-atom) is an eigenfunction. If it is, then also give the eigenvalue.
a. $-\left(\mathrm{h}^{2} / 2 \mathrm{n}_{\mathrm{e}}\right) \nabla^{2}-\mathrm{e}^{2 / r}$
yes

$$
E_{n=2}=\frac{-e^{2}}{8 a_{0}}
$$

$$
\text { (1) }\left(\text { or } \frac{-e^{2}}{32 \pi \varepsilon_{0} a_{0}}\right)
$$

b. $\hat{L}_{+}$
No
$2 P_{y}=-\frac{\text { linear combination of }}{4_{211}}$

$$
\begin{equation*}
m l=+1 \quad m P=-1 \tag{2}
\end{equation*}
$$

c. $\hat{i}^{2}$

```
(1)
            Yes
```

$$
\begin{aligned}
& l(l+1) \hbar^{2}=1(1+1) \hbar^{2}=2 \hbar^{2} \\
& L^{2}=2 \hbar^{2}
\end{aligned}
$$

II. $2(11 \%)$ Consider the 2 s electron of the H atom. Prove that the expectation value of the potential energy $\langle\mathrm{V}\rangle=2\langle\mathrm{E}\rangle$, where $\langle\mathrm{E}\rangle$ is the expectation value of the total energy.

$$
\Psi_{200}=\frac{1}{\sqrt{32 \pi}}\left(\frac{1}{a_{0}}\right)^{3 / 2}\left(2-\frac{r}{a_{0}}\right) \exp \left(-r / 2 a_{0}\right)
$$

$$
\begin{aligned}
& \Psi_{200}=\frac{1}{\sqrt{32 \pi}}\left(\frac{1}{a_{0}}\right)^{3 / 2}\left(2-\frac{r}{a_{0}}\right) \exp \left(-r / 2 a_{0}\right) \\
& \langle E\rangle=E_{2}=-\frac{e^{2}}{8 a_{0}} \quad\left(0 r-\frac{e^{2}}{8 \pi \varepsilon_{0} a_{0} \cdot 4}=-\frac{e^{2}}{32 \pi \varepsilon_{0} a_{0}}\right) \text { : the expectation value } \begin{array}{l}
\text { frenergy is the } \\
\text { eigenvalue } E n=2
\end{array}
\end{aligned}
$$

${ }^{b}\langle V\rangle=\int H_{200}^{*} \hat{V} H_{200} d \tau$ $V=-\frac{e^{2}}{r \varepsilon_{0}}$ or $V=-\frac{e^{2}}{r}$. take $V=-\frac{e^{2}}{r}$

$$
v\rangle=\int_{0}^{\infty} 4 x_{200}^{2}\left(-\frac{e^{2}}{r}\right) \cdot 4 \pi r^{2} d r=-\frac{4 \pi e^{2}}{32 \pi a_{0}^{3}} \int_{0}^{\infty}\left(2-\frac{r}{a_{0}}\right)^{2} r \exp -\frac{r}{a_{0}} d r
$$

$$
\begin{aligned}
& 7=\int_{0} 4 x_{200}^{2}\left(\frac{-e^{2}}{r}\right) \cdot 4 \pi r^{2} d r=-\frac{4 \pi}{32 \pi a_{0}^{3}} 0_{0}^{\infty} \frac{e^{2}}{8 a_{0}^{3}} \int_{0}^{\infty}\left(4+\frac{r^{2}}{a_{0}^{2}}-\frac{4 r}{a_{0}}\right) r \exp -\frac{r}{a_{0}} d r=\frac{-e^{2}}{8 a_{0}^{3}} \int_{0}^{\infty}\left(4 r+\frac{r^{3}}{a_{0}^{2}}-\frac{4 r^{2}}{a_{0}}\right) \exp -\frac{r}{a_{0}} d r \\
& \left.1 \quad 3!-\frac{2!}{11^{3}}\right]
\end{aligned}
$$

$$
=-\frac{e^{2}}{8 a_{0}^{3}}\left[4 \cdot \frac{1}{\left(\frac{1}{a_{0}}\right)^{2}}+\frac{1}{a_{0}^{2}} \frac{3!}{\left(\frac{1}{a_{0}}\right)^{4}}-\frac{4}{a_{0}} \frac{2!}{\left(\frac{1}{a_{0}}\right)^{3}}\right]
$$

$$
\begin{aligned}
& =-\frac{e^{2}}{8 a_{0}^{3}}\left[\left(\frac{1}{a_{0}}\right)^{2}\right. \\
& =\frac{-c^{2}}{8 a_{0}^{3}}\left[4 a_{0}^{2}+6 a_{0}^{2}-8 a_{0}^{2}\right]=\frac{-e^{2}}{4 a_{0}}=2\left(-\frac{e^{2}}{8 a_{0}}\right)=2\langle E\rangle
\end{aligned}
$$

$$
\text { or } \left.\begin{array}{rl}
\langle V\rangle & =-\frac{e^{2}}{16 \pi \varepsilon_{0} a_{0}} \\
\langle E\rangle=E_{2}=\frac{-e^{2}}{32 \pi \varepsilon_{0} a_{0}}
\end{array}\right\} \Rightarrow\langle V\rangle=2\langle E\rangle
$$

III. 3 ( $12 \%$ ) Consider the Hydrogen atom in the 1 s state:

$$
\Psi_{100}=\frac{1}{\sqrt{\pi}}\left(\frac{1}{a_{0}}\right)^{3 / 2} \exp \left(-r / a_{0}\right)
$$

a. Calculate the value of $r$ at the classical turning point (in terms of $\mathrm{a}_{0}$ ).
the classical turning point occurs (when $E<V$ : classically for bidden region)
$E=V$ is turning paint
$\eta^{2 a_{0}} \frac{-e^{2}}{2}=\frac{e^{2}}{r} \Rightarrow r=2 a_{0}$ classical turing point
at $r>20.0$, classically forbidden region
b. Calculate the percentage of electric charge present beyond the classical turning point. change beyond the classical turning point = probability of electric charge beyond the $r=2 a_{0}$ (ie, $r>2 a_{0}$ ). $=\int_{200}^{\infty} \psi_{100}^{*} \psi_{100} d \tau=1-\int_{0}^{200} 4 \psi_{100}^{*} \psi_{100} d \tau=1-\int_{0}^{200} 4100^{2} d \tau$ $\int_{0}^{2 a 0} 44_{100}^{2} d \tau=\frac{4 \pi}{\pi} \cdot \frac{1}{a_{0}^{3}} \cdot \int_{0}^{2 a a_{0}} r^{2} \exp -\frac{2 r}{a_{0}} d r=\frac{4}{a_{0}^{3}} \int_{0}^{2 a_{0}}\left(-\frac{a_{0}}{2}\right) r^{2} \exp -\frac{2 r}{a_{0}} \cdot d-\frac{2 r}{a_{0}}$
$=\frac{4}{a_{0}{ }^{3}}\left(-\frac{a_{0}}{2}\right)\left[r^{2} \exp -\left.\frac{2 r}{a_{0}}\right|_{0} ^{2 a_{0}}-\int_{0}^{2 a 0} \exp -\frac{2 r}{a_{0}} \cdot d r^{2}\right]=$
$=-\frac{2}{a_{0}^{2}}\left[r^{2} \exp -\left.\frac{2 r}{a_{0}}\right|_{0} ^{2 a_{0}}-\int_{0}^{2 a 0} 2 r \cdot\left(-\frac{a 0}{9}\right) \cdot \exp -\frac{2 r}{a_{0}} \cdot d-\frac{2 r}{a_{0}}\right.$
$=-\frac{2}{a_{0}{ }^{2}}\left[r^{2} \exp -\left.\frac{2 r}{a_{0}}\right|_{0} ^{2 a_{0}}+a_{0}\left(r \exp -\left.\frac{2 r}{a_{0}}\right|_{0} ^{2 a 0}-\int_{0}^{2 a 0} \exp -\frac{2 r}{a_{0}} d r\right.\right.$
$=-\frac{2}{a_{0} 2^{2}}\left[r^{2} \exp -\left.\frac{2 r}{a_{0}}\right|_{0} ^{2 a_{0}}+a_{0} r \exp -\left.\frac{2 r}{a_{0}}\right|_{0} ^{2 a_{0}}-a_{0} \cdot\left(-\frac{a_{0}}{2}\right) \cdot \exp -\left.\frac{2 r}{a_{0}}\right|_{0} ^{2 a_{0}}\right.$
$=-\frac{2}{a_{0}^{2}}\left(4 a_{0}^{2} e^{-4}+2 a_{0}^{2} e^{-4}+\frac{a_{0}^{2}}{2} e^{-4}-\frac{a_{0}^{2}}{2}\right)=8 e^{-4}-4 e^{-4}-e^{-4}+1 \quad 6$
$\begin{aligned}=1.13 e^{-4} \Rightarrow \int_{2 a_{0}}^{\infty} 4 x_{100}^{2} d r=1-\left(1-13 e^{-4}\right) & =13 e^{-4}=0.238 \\ & \Rightarrow 23.8 \% \text { electric charge (e). }\end{aligned}$
III. 4 ( 12 \%) Consider a wavefunction $\Psi(\mathrm{x}, \mathrm{t})$ for a one-dimensional system that is the superposition of two stationary-state wavefunctions with energies $E_{1}$ and $E_{2}$, i.e.,.:
$\Psi(x, t)=a \exp \left(-i E_{1} t / \hbar\right) \Psi_{1}(x)+b \exp \left(-i E_{2} t / \hbar\right) \Psi_{2}(x)$
where $\Psi_{1}(\mathrm{x})$ and $\Psi_{2}(\mathrm{x})$ are real orthonormal spatial eigenfunction that obey the relations:

$$
\int \Psi_{1}(x)^{2} d x=\int \Psi_{2}(x)^{2} d x=1 ; \int \Psi_{1}(x) \Psi_{2}(x) d x=0
$$

(a) Show that for $\Psi(\mathrm{x}, \mathrm{t})$ to be normalized the constants a and b must obey $\mathrm{a}^{2}+\mathrm{b}^{2}=1$
$\int \psi(x, t)^{x} \psi(x, t) d x=\int\left[a \exp i E_{1} t\left(\hbar \psi_{1}(x)+b \exp i E_{2} t / \hbar \psi_{2}(x)\right]\left[a \exp -i F_{1} t / \hbar \psi_{1}(x)\right.\right.$ $\left.+b \exp -i E_{2} t / \hbar_{1} Y_{2}(x)\right] d x=\int a^{2} Y_{1}^{2}(x)+a b \exp i E_{1} t / \hbar \cdot \exp -i E_{2} t / \hbar_{1} \psi_{1}(x) \cdot \psi_{2}(x)+$ $b$ a expiE2t/h. exp-iE1t/万 $\left.\psi_{2}(x) \cdot \psi_{1}(x)+b^{2} \psi_{2}^{2}(x)\right) d x$
$a^{2} \int \psi_{1}^{2} d x+a b \exp \frac{i t}{\hbar}\left(E_{1}-E_{2}\right) \int \psi_{1} \psi_{2} d x+b a \exp \frac{i t}{\hbar}\left(E_{2}-E_{1}\right) \int \psi_{1} \psi_{2} d x$ $+b^{2} \int 4_{2}^{2} d x=a^{2}(1)+0+0+b^{2}(1)=a^{2}+b^{2} \Rightarrow \quad a^{2}+b^{2}=1$
(b) Show that the probability $|\Psi(x, t)|^{2}$ varies in time according to:

$$
|\Psi(x, t)|^{2}=a^{2} \Psi_{1}(x)^{2}+b^{2} \Psi_{2}(x)^{2}+2 a b \Psi_{1}(x) \Psi_{2}(x) \cos \left[\left(E_{1}-E_{2}\right) t / \hbar\right]
$$

$\left.V(x, t)\right|^{2}=\psi(x, t)^{*} \psi(x, t)=a^{2} \psi_{1}{ }^{2}+a b \psi_{1} \psi_{2} \exp \frac{i t}{\hbar}\left(E_{1}-E_{2}\right)+b a \psi_{2} \psi_{1} \exp \frac{i t}{\hbar}\left(E_{2}-E_{1}\right)$,
$\cdot b^{2} U_{2}(x)=a^{2} H_{1}(\lambda)^{2}+b^{2} \psi_{2}(x)^{2}+a b U_{1}(x) \Psi_{2}(x)\left[\exp \frac{i t}{\hbar}\left(E_{1}-E_{2}\right)+\exp -\frac{i t}{\hbar}\left(E_{1}-E_{2}\right)\right]$ - $a^{2} U_{1}(x)^{2}+b^{2} U_{2}(x)^{2}+a b \psi_{1}(x) \cdot U_{2}(x)\left[\cos \frac{t}{\hbar}\left(E_{1}-E_{2}\right)+i \sin \frac{t}{\hbar}\left(E_{1}-E_{2}\right)+\right.$ $\left.\cos \frac{t}{\hbar}\left(E_{1}-E_{2}\right)-i \sin \frac{t}{\hbar}\left(E_{1}-E_{2}\right)\right]=a^{2} H_{1}(x)^{2}+b^{2} H_{2}(k)^{2}+2 a b \cos \frac{t}{\hbar}\left(E_{1}-E_{2}\right)$.
(c) For which values of a and b is $\Psi(\mathrm{x}, \mathrm{t})$ a stationary state of the system
$\psi(x, t)$ stationary state of the system $\Rightarrow$ prohahi itiy does') (hinge with tine $\Rightarrow|\psi(x, t)|^{2}$ is nd a $f(t) \Rightarrow 2 a b \cos \frac{t}{\hbar}\left(E_{1}-E_{2}\right)=0$

$$
\Rightarrow a=0 \quad a \quad b=0
$$

III. 5 ( $15 \%$ ) Let $\mid n 1 m>$ refer to the (orthonormal) energy wavefunctions of the H atom $\psi_{\mathrm{n} / \mathrm{m}}$. Consider a system described by the following wavefunction $\Psi$ :

$$
\Psi=\frac{1}{\sqrt{5}}|300\rangle+\frac{1}{\sqrt{5}}|320\rangle+\frac{1}{\sqrt{5}}|310\rangle+\frac{1}{\sqrt{5}}|311\rangle+\frac{1}{\sqrt{5}}|31-1\rangle
$$

i. What is the expectation value of the energy for this state? (expressed in terms of $\mathrm{e}^{2 / a_{0}}$ ) $\langle E\rangle=E_{3}$ : the eigenvalue. because the warefunctions are degeneate $E_{3}=\frac{-e^{2}}{2 a_{0} \cdot n^{2}}=\frac{-e^{2}}{2 a_{0} \cdot 9}=-\frac{e^{2}}{18 a_{0}}$
ii. What is the expectation value of the orbital angular momentum for this state? $\hat{L}^{2} \Psi=\hbar^{2} l(l+1) \Psi$ $\left\langle L^{2}\right\rangle=\frac{1}{5} \cdot 0+\frac{1}{5} \cdot \hbar^{2}(2)(3)+\frac{1}{5} \cdot \hbar^{2}(1)(2)+\frac{1}{5} \hbar^{2}(1)(2)+\frac{1}{5} \hbar(1)(2)$
$=\frac{\hbar^{2}}{5}(6+2+2+2)=\frac{12 \hbar^{2}}{5}:$
iii. What is the expectation value of the z-component of the orbital angular momentum? $\hat{L}_{2} W_{=} m_{e} \hbar 4$ $\left\langle\langle z\rangle=\frac{1}{5} \cdot 0+\frac{1}{5} \cdot 0+\frac{1}{5} \cdot 0+\frac{1}{5} \cdot(\hbar)+\frac{1}{5}(-\hbar)=0\right.$
iv. What is the probability that a measurement of the orbital angular momentum is 0 ?

$$
\begin{gathered}
\text { probability that } L=0 \text { then } L^{2}=0 \Rightarrow \frac{1}{5} \\
\Rightarrow=0
\end{gathered}
$$

v. What is the probability that a measurement of the $z$-component of the orbital angula: momentum is 0

$$
\begin{aligned}
& \text { probabilility that } L z=0 \Rightarrow m e=0 \\
& \Rightarrow \frac{1}{5}+\frac{1}{5}+\frac{1}{5}=\frac{3}{5}
\end{aligned}
$$

a.

$$
\begin{aligned}
\hat{H}= & -\frac{\hbar^{2}}{2 m}\left(\frac{1}{r^{2}} \frac{\partial}{\partial r} r^{2} \frac{\partial}{\partial r}+\frac{1}{r^{2} \sin \theta} \frac{\partial}{\partial \theta}\left(\sin \theta \frac{\partial}{\partial \theta}\right)+\frac{1}{r^{2} \sin ^{2} \theta} \frac{\partial^{2}}{\partial \phi^{2}}+\frac{e^{2}}{r}\right. \\
\hat{H} Y_{e}^{m e}(\theta, \phi)= & -\frac{\hbar^{2}}{2 m}\left(\frac{1}{r^{2} \sin \theta} \frac{\partial}{\partial \theta}\left(\sin \theta \frac{\partial}{\partial \theta}\right)+\frac{1}{r^{2} \sin ^{2} \theta} \frac{\partial^{2}}{\partial \phi^{2}}\right) Y_{e}^{m}(\theta, \phi) \\
& +\frac{e^{2}}{r} Y_{e}^{m e}(\theta, \phi) \\
= & \frac{\hat{L}^{2}}{2 I} Y_{e}^{m}(\theta, \phi)+\frac{e^{2}}{r} Y_{e}^{m}(\theta, \phi) \\
= & \frac{\hbar^{2}}{2 I} l(l+1) Y_{e}^{m}+\frac{e^{2}}{r} Y_{e}^{m} \\
& \left(r \text { constent)}=\left(\frac{\hbar^{2}}{2 I} l(l+1)+\frac{e^{2}}{r}\right) Y_{e}^{m}(\theta, \phi) \Rightarrow\right. \text { yes, an eiugenfendion }
\end{aligned}
$$

b. $\hat{L}^{2} Y_{e}^{m l}=\hbar^{2} l(l+1) Y_{e}^{m e} \quad \Rightarrow$ yes, an eigenfunction
c. $\hat{L}_{z} Y_{e}^{m e}=m e \hbar Y_{e}^{m e} \quad \Rightarrow$ yes "
d. $\frac{\hat{L}^{2}}{2 I} Y_{e}^{m e}=\frac{\hbar^{2} l(\ell+1)}{2 I} Y_{e}^{m}$

