CEM 882 Lectures 6

Quantum mechanics





particle y p^{+} $p^$ $\frac{2I}{(\Psi,t)} = \int \frac{1}{2\pi} \frac{e^{ik\Psi}}{e^{ik\Psi}} \frac{e^{ik\Psi}}{time} \frac{1}{\sqrt{2\pi}} \frac{e^{ik\Psi}}{e^{i\omega_k t}}$ Classical Mechanics 4(t)=4(0)+wt $P(g',t') = \mathcal{I}(g',t') \mathcal{I}^{*}(g',t') =$ | ₹(g', t')|² complex (i→-i) real meginary conjugate M = a+ib ≡ complex nonber probability specific values imaginary(i) $M \times M^* = (a+ib)(a-ib)_{12}$ $\vec{M} = |\vec{M}|(\omega s \theta + i sin \theta) = |\vec{M}|^2$ a real $\vec{M} = |\vec{M}|(\omega s \theta + i sin \theta) = |\vec{M}|e^{i\theta}$ Euler relationship Euler relationship Euler relationship (from Taylor expen) also true wave Function

 $IP(\varphi',t') = \frac{1}{2\Pi}e^{ik\varphi'} - i\omega t' - ik\varphi' i\omega t$ $\underline{\underline{Y}}(\varphi',t')$ $\underline{\underline{Y}}(\varphi',t')$ specific values of $e^{A}e^{B}=e^{A+B}e^{O}=1$ 4 and t = _ => independent of 4', t', k consistent se is always equally with q-indep dispersed around orbit(ring) endent potential $SP(\vec{g})d\vec{g} = 1 = S\mathcal{I}(\vec{g})\mathcal{I}(\vec{g})d\vec{g}$ all particle Normalized positions integrated probability or just one particle nd position 2 Postulate (Law) of g.m. Every measurable (observeable) unique Hermitian => see property has a mathematical notes operator/expre A => A = = a = value of ssion property no lecule = Particle position operators are classical mechanics positions e.g. x, y, z

Momentum = Px, Py, Pz Linear $P_{x} = mv_{x} = m^{d_{x}}dt$ $P_{y} = mv_{y} = m^{d_{y}}dt$ $P_{z} = mv_{z} = m^{d_{z}}dt$ ive_{s} C.H. ⇒ $Q.M. \Rightarrow P_{x} = -ih \frac{d}{d_{x}} \frac{position}{derivatives}$ $P_{y} = -ih \frac{d}{d_{z}} \frac{derivatives}{derivatives}$ $P_{z} = -ih \frac{d}{d_{z}} \frac{derivatives}{dz}$

Electric field of radiation of $\mathcal{E}(x) = \mathcal{E}_0 \cos(2\pi kx) = \mathcal{E}_0 e^{2\pi i kx} (real)$ De Broglie => Px = h = hk k= wavenum $-i\hbar \frac{\partial}{\partial y} e^{2\pi i k x} = (-i\hbar)(2\pi i k) e^{2\pi i k x} e^{-i\hbar}$ $A 4 = hk e_0 e^{2\pi i k x} (h)(2\pi) e^{-i\hbar}$ $A 4 = hk e_0 e^{-i\hbar}$

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 $\vec{h} = \vec{r} \times \vec{p} \not\in -i\hbar \left(\frac{1}{3\chi} \div \frac{1}{3y} \div \frac{1}{3z} \div \frac{1}{3\chi} \right)$ $\times \hat{x} + y \div \hat{y} + \hat{z} \stackrel{2}{\hat{z}}$ $\chi = r \cos \varphi Z Radial atom$ $y = r \sin \varphi \sum r, \ell, z cylindrical coordinates$

 $L_z = -i\hbar \frac{1}{3\varphi}$

 $L_{2} \int_{2\pi}^{L} e^{ik\varphi} = \hbar k \int_{2\pi}^{L} e^{ik\varphi}$ eigenvalue eigenfunction of L_{2} for radial atom

Third postulate of g.m.

Only values of a property are the

eigenvalues of the operator

on the eigenfunction of the system (molecule) => Values of Lz for sodial atom are Tike Bra (ket short hand notation (see notes)) 7 = ket (not displayed (= bra (implicit, complex (*) conjugate => i ->-i)

< 1 > = integration over all positional space

Math \Rightarrow order of operators and/or wave functions can be switched for simple orithmetic multiplication but not if there are derivatives $\chi \stackrel{1}{\Rightarrow} \chi = \chi \stackrel{\text{Switch}}{\text{order}} \stackrel{1}{\Rightarrow} \chi^2 = 2\chi$

If wavefunction is eigenfunction of operator, measurement of property is eigenvalue $24 = \int_{2\pi}^{1} e^{2i\varphi}$ $L_2 \Rightarrow -i\hbar \frac{3}{3\varphi} \int_{2\pi}^{1} e^{2i\varphi} = 2\hbar \int_{2\pi}^{1} e^{2i\varphi}$ Otherwise, were function can always be expressed as sum = linear combination of eigenfunctions of ate 127 = S, Cj(φ;) ¢; = tineger integer math j= integer mine eigennal complex number ues and eigennal In general, φ; ore orthonormal func 2π, * $\int \phi_j^* \phi_j d\varphi = 1 \quad \int \phi_k^* \phi_j d\varphi = 0 \quad (j \neq k)$ orthogonal king {\$\$\$K\$ (\$\$) = \$Kj De probab ility normalized after integration over all positional space



Average measurel value of property, when system is represented by $2f = \sum_{j \neq j} \phi_{j}$ $= \langle 4|A|4\rangle = \sum_{k} \langle \phi_{k}|c_{k}^{*}A E_{i}c_{j}|\phi_{j}\rangle$ $= \sum_{k} \langle \phi_{k} | c_{k}^{*} \leq \lambda_{j} c_{j} | \phi_{j}^{*} \rangle$ $= \sum_{k} \sum_{j} c_{k}^{*} c_{j}^{*} \lambda_{j}^{*} \langle \phi_{k} | \phi_{j}^{*} \rangle$ = Solckliz R Probability-weighted K R R eigenverves not an eigenverves For example from previous page, $\left\{ L_{2} \right\} = \frac{16}{25} \left(-h \right) + \frac{9}{25} \left(t \right) = \frac{-7}{25} h$ Probability-weighted average

Time-dependence of wavefunction

Fifth postulate of g.m.

- Total Energy operator E guation = T + V 5 T potential Hamiltonian Energy operator operator

Electric field of radiation

- $\mathcal{E}(\mathbf{t}) = \mathcal{E}_{o}\cos(\mathbf{wt}) = \mathcal{E}_{o}e^{-i\mathbf{wt}}\left(\frac{real}{port}\right)$
- $i\hbar \frac{dE}{dt} = \hbar w E_0 e^{-iwt}$ dt photon energy

T = Kinetic energy operator $\frac{1}{2}mv^{2} = \frac{1}{2}m(v_{x}^{2} + v_{y}^{2} + v_{z}^{2})$ $=\frac{1}{2m}\left((mv_{x})^{2}+(mv_{y})^{2}+(mv_{z})^{2}\right)$ $= \frac{1}{2m} \left(P_{x}^{2} + P_{y}^{2} + P_{z}^{2} \right) P_{x} = -i\pi \frac{1}{2m} \left(P_{x}^{2} + P_{y}^{2} + P_{z}^{2} \right)$ $= -\frac{\hbar^2}{2m} \left(\frac{J^2}{J\chi^2} + \frac{J^2}{Jy^2} + \frac{J^2}{Jz^2} \right) \frac{\text{Repeat}}{\text{for}}$ Radial atom $\frac{1}{2}mv^{2} = \frac{1}{2}\left(\frac{mvr}{r}\right)^{2} = \frac{1}{2}\left(\frac{mvr}{r}\right)^{2} = \frac{1}{2}\left(\frac{mvr}{r}\right)^{2}$ h22 2mr² IF moment of identia (number) V = Potential energy operator(of ten class.mech. pot.energy expression) $Vradial atom = <math>\left(\frac{L}{4\pi\epsilon_0}\right) \frac{e^2}{r}$ (constant)

IFV is time-independent I(g) Z(g) = EZ(g) independent energy (AE Schroding eigen value (observed Equation in spectra)

Radial atom $-\frac{\hbar^2}{2T}\frac{3^2 4}{3 \varphi^2} - \left(\frac{1}{4\pi\epsilon_0}\right)\frac{e^2}{r^2} - \frac{2}{4} = E^2$ - \hbar^2 J^2 ZI J^2 = T^2 $T^$ 24 = J_I eik 4 integer $T = h^2 k^2$ 2I $E = \frac{\hbar^2 k^2}{2 \mathrm{I}} - \left(\frac{1}{4 \mathrm{II} \varepsilon_0}\right) \frac{e^2}{c}$





Time-dependence of 7 when ket is fine-independent $\begin{aligned} & \exists (\hat{g}, \xi) &= \underbrace{\sum_{j=1}^{n} C_j(\xi) | \phi_j(\hat{g}) + \underbrace{\sum_{j=1}^{n} V_j(\xi) | \phi_j(\xi) \\ &= \underbrace{\sum_{j=1}^{n} V_j(\xi) | \phi_j(\xi) | \phi_j(\xi) | \phi_j(\xi) \\ &= \underbrace{\sum_{j=1}^{n} V_j(\xi) | \phi_j(\xi) | \phi_j(\xi) | \phi_j(\xi) | \phi_j(\xi) \\ &= \underbrace{\sum_{j=1}^{n} V_j(\xi) | \phi_j(\xi) | \phi_$ $\begin{aligned} & \sum_{j} i \hbar \frac{dc_{j}}{dt} \langle \Phi_{k} | \Phi_{j} \rangle = \sum_{j} c_{j} \langle \Phi_{k} | \mathcal{F}_{j} | \Phi_{j} \rangle \\ & \int_{\mathcal{K}} \frac{dc_{k}}{dt} \sum_{j} \frac{dc_{j}}{dt} \sum_{j} \frac{c_{j} | \Phi_{j} \rangle}{\int_{\mathcal{K}} \frac{dc_{k}}{dt}} \\ & \sum_{j=k} \frac{c_{j} | \Phi_{j} \rangle}{\int_{\mathcal{K}} \frac{dc_{k}}{dt}} \\ & \sum_{j=k} \frac{c_{j} | \Phi_{j} \rangle}{\int_{\mathcal{K}} \frac{dc_{k}}{dt}} \\ & \sum_{j=k} \frac{c_{j} | \Phi_{j} \rangle}{\int_{\mathcal{K}} \frac{c_{k}}{dt}} \\ & \sum_{j=k} \frac{c_{j} | \Phi_{j} \rangle}{\int_{\mathcal{K}} \frac{c_{j} | \Phi_{j} \rangle}{\int_{\mathcal{K}} \frac{c_{j} | \Phi_{j} \rangle}{\int_{\mathcal{K}} \frac{c_{j} | \Phi_{j} \rangle}{\int_{\mathcal{K}} \frac{c_{$

Time-dependent Schrodinger Equation





If 24 is a single ligenfunction energy or sum of reigenfunctions

with the same energy,

average values of all measureable

properties are time-independent



Radiative transitions of radial about

Transition from $|\phi_j\rangle \rightarrow |\phi_k\rangle$ $\int \mathcal{F}(t) \approx |\phi_j\rangle + C_k(t) |\phi_k\rangle$ $\int \mathcal{F}(t) \approx |\phi_j\rangle + C_k(t) |\phi_k\rangle$ $\mathcal{F}(t) = 0$

Part of Hamiltonian which causes transitions is Il' = - IL. Eradiation $\vec{\mu} = -er(\cos \varphi \hat{x} + \sin \varphi \hat{y})$ $\vec{E}_{rad} = \vec{E}_{o} \cos \omega_{rt} \hat{\chi} \equiv \vec{E}_{o} \vec{e}^{i\omega_{rt}} \hat{\chi}$ Real part - ju. Érad = -er Eo cos Qe i wrt time-so can Time-dep. S.E. A=-ju Eo Cause trans tions $\frac{dc_k}{dt} |\phi_k\rangle = -\frac{i}{\hbar} A \cos \varphi = \frac{i}{(10)} + \frac{c_k |\phi_k\rangle}{h}$ Project $\langle \Phi_k | \Rightarrow \cos \varphi = e^{i\varphi} + e^{-i\varphi}$

 $\frac{dc_{k}}{dt} = \frac{iAe}{2\pi} \left(\langle \phi_{k} | e^{i\phi} | \phi_{j} \rangle + \langle \phi_{k} | e^{-i\phi} | \phi_{j} \rangle \right)$ dipole moment CKSOR(e'IDK)+CKSORJE'9 $\frac{1}{2\pi}\int e^{-ik\varphi} e^{i\varphi} e^{-ik\varphi} d\varphi = \frac{1}{2\pi}\int e^{i\varphi} d\varphi$ $=\frac{1}{2\pi}\left(\begin{array}{c} S\cos\varphi d\varphi + iS\sin\varphi d\varphi\right) = 0$ $\begin{array}{c} 2\pi \\ 3 \frac{1}{2\pi} \int -i k \varphi i \varphi i \varphi \\ 2\pi \int e e e e d \varphi \\ 2\pi \int 2\pi \int \varphi \\ 2\pi \int 2\pi \int 2\pi \int 2\pi$ $= \frac{1}{2\pi} \int_{e}^{2\pi} (j-k+i)\varphi = \frac{2\pi}{d\varphi} = \frac{2\pi}{2\pi} \int_{e}^{2\pi} d\varphi = 1$ If j-k+i=0Selection rule => e integral (non zero trans. app. mon.) gives j-k-1=0 Overall selection rule K-j=ti => transition. dipole moment = { \$ 1 ue 10; >= w

Selection rule =

Mathematical

Alationship between





dipole noment is

Non-zero

Recall that energy eigenstate 10j) has time dependence e-iwjt where wj = tJ/h $\langle \hat{e}^{i\omega_{k}t} | e^{ii\varphi} | \phi_{j} \hat{e}^{i\omega_{j}t} \rangle = e^{i(\omega_{k} - \omega_{j})t} \text{ for } \omega_{kj} \equiv k - j = \pm 1$ spatial (4) contrined Bohr frequency $\frac{dc_{k}}{dt} = \frac{-iA}{h} e^{i\omega_{k}jt} - \frac{i\omega_{r}t}{e} e^{-i\omega_{r}t}$ $= -iA e^{i(\omega_{kj}-\omega_{r})t}$ transition th oscillatory except dipole dipole der de la trifice when weight trifice when weight electric Resonance field SE E photon E is dipower with molecule photon E is dipower with molecule species to the transition of radiation, us no lecule-speci