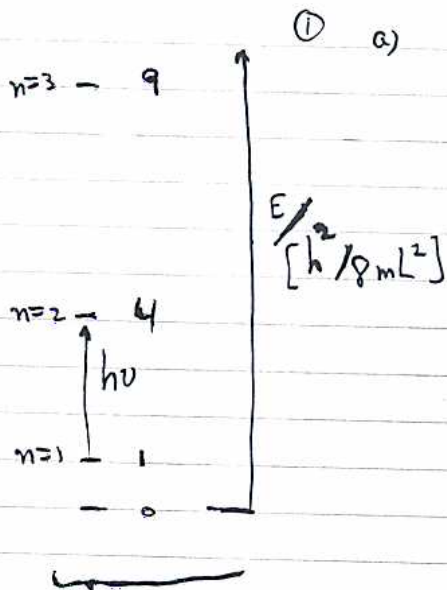


Chem. 1480, Final Exam Solutions, 4/07



$$h\nu = E_2 - E_1 = \frac{h^2}{8mL^2} (2^2 - 1^2)$$

↑
frequency of light absorbed in transition from $n=1 \rightarrow n=2$

Thus,

$$\nu = \frac{3h}{8mL^2}$$

Energy level ladder for particle of mass m , in a 1D box of length L

b) unit normalized: $\psi_1(x) = \sqrt{\frac{2}{L}} \sin(\pi x/L)$

$$\psi_2(x) = \sqrt{\frac{2}{L}} \sin(2\pi x/L)$$

then $I_{21} = a_{21}^2$, with

$$a_{21} = \frac{2}{L} \int_0^L x \sin\left(\frac{\pi x}{L}\right) \sin\left(\frac{2\pi x}{L}\right) dx = -\frac{L}{\pi^2} \cdot \frac{16}{9}$$

$\swarrow i=1$ $\searrow i=2$

we given
integral identity \rightarrow

$$\frac{-L}{\pi^2} \left[\frac{1}{1^2} - \frac{1}{3^2} \right]$$

$\underbrace{\hspace{2cm}}_{\frac{8}{9}}$

finally:

$$I_{21} = \frac{L^2}{\pi^4} \left(\frac{16}{9}\right)^2$$

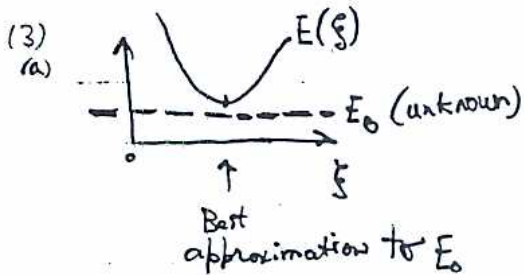
2

(a) $\psi_0(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{-m\omega x^2/2\hbar}$; $E_0 = \frac{1}{2}\hbar\omega$
 $\psi_1(x) = \frac{1}{\sqrt{2}} \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} H_1\left(\sqrt{\frac{m\omega}{\hbar}} x\right) e^{-m\omega x^2/2\hbar}$; $E_1 = \frac{3}{2}\hbar\omega$ } corresponding energy eigenvalues

(b) $\psi_1(x) = \frac{1}{\sqrt{2}} \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} H_1\left(\sqrt{\frac{m\omega}{\hbar}} x\right) e^{-m\omega x^2/2\hbar}$, or $H_1(y) \equiv 2y =$ Hermite polynomial H_1

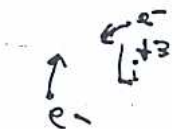
(c) $P_0 \equiv$ Probability that a measurement of energy yields $E_0 = (.949)^2 = \boxed{0.9}$

$P_1 = (.316)^2 = \boxed{0.1}$; $P_2 = \boxed{0}$



So set $0 = \frac{dE}{dx} \Rightarrow \boxed{\xi_m = \frac{43}{16}}$

(b) $2 < \xi_m < 3$



This electron sees the Li^{+3} nucleus partially shielded by

the other electron, hence an effective nuclear charge < 3 .

2

(4) (a) $\alpha \equiv \int d\tau \psi_i \hat{H} \psi_i$; $i = A, B, C$; \hat{H} = effective 1-electron Hückel Hamiltonian operator

↑
"Coulomb Integral"

↑
[In practice this operator is never explicitly defined;
the value of α is estimated by semi-empirical arguments.]

$$\beta \equiv \int d\tau \psi_A \hat{H} \psi_B = \int d\tau \psi_B \hat{H} \psi_A = \int d\tau \psi_A \hat{H} \psi_C \leftarrow \text{"Resonance Integral"}$$

E = Molecular Orbital Energy eigenvalue.

(ii) In simple Hückel theory $\beta = 0$ for interactions between non-nearest neighbors. Hence here:

$$\int d\tau \psi_A \hat{H} \psi_C = \int d\tau \psi_C \hat{H} \psi_A = 0$$

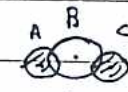
(b) Looking down from top:

$$\begin{bmatrix} 1 \\ \sqrt{2} \\ 1 \end{bmatrix}$$



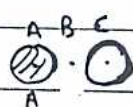
↑
hatched marks
indicate + lobe

$$\begin{bmatrix} 1 \\ -\sqrt{2} \\ 1 \end{bmatrix}$$



↑
negative

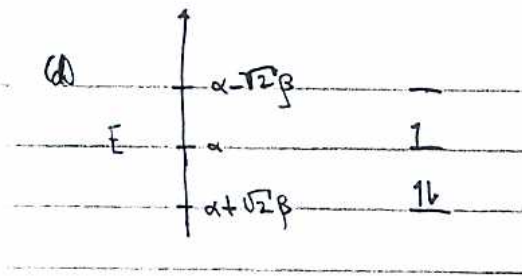
$$\begin{bmatrix} 1 \\ 0 \\ -1 \end{bmatrix}$$



(c)

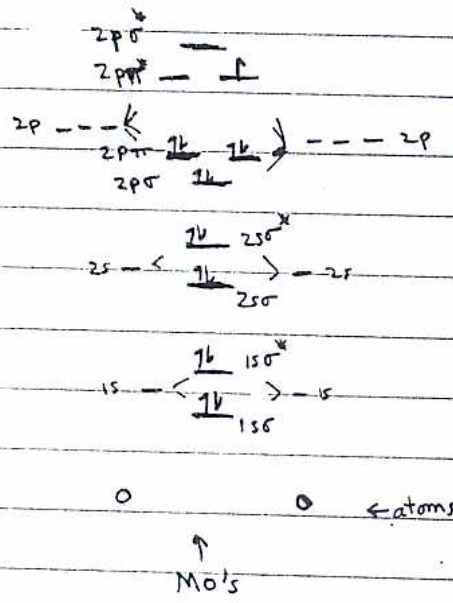
$$\begin{bmatrix} \alpha & \beta & 0 \\ \beta & \alpha & \beta \\ 0 & \beta & \alpha \end{bmatrix} \begin{bmatrix} 1 \\ \pm\sqrt{2} \\ 1 \end{bmatrix} = \alpha \pm \sqrt{2}\beta \begin{bmatrix} 1 \\ \pm\sqrt{2} \\ 1 \end{bmatrix} ; \begin{bmatrix} \alpha & \beta & 0 \\ \beta & \alpha & \beta \\ 0 & \beta & \alpha \end{bmatrix} \begin{bmatrix} 1 \\ 0 \\ -1 \end{bmatrix} = \alpha \begin{bmatrix} 1 \\ 0 \\ -1 \end{bmatrix}$$

③



↑ ground state
π-electron configuration
in the allyl radical

(5)



Assuming "polarity" distortions are small, NO MO diagram should closely resemble that for O_2 (shown).

then, the only effect of NO vs. O_2 is the # of electrons.

[p. Atkins P. 375]; actually it makes no difference here whether $2p\sigma$ or $2p\pi$ is lower

(i) For NO, #electr = 15 (see

diagram) ⇒ Bond order = $2\frac{1}{2}$

(ii) For NO^+ , #electr = 14 ⇒

Bond order = 3

(6) Key point: $\psi(1,2) = \psi(2,1)$ for consistency w/ modified Pauli Exclusion Principle

Thus: (i) not OK [$\psi(1,2) = -\psi(2,1)$]

(ii) OK

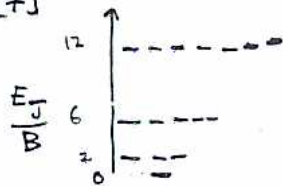
(iii) not OK [$\psi(1,2) = -\psi(2,1)$]

(iv) not OK [neither symmetric nor antisymmetric w.r.t. $1 \leftrightarrow 2$ exchange]

(v) OK

(4)

[7]



Rigid Rotor Energy Levels
(Including Degeneracy: $2J+1$)

Thus, in

$$I_{J \rightarrow J+1} = (2J+1) e^{-J(J+1)B/k_B T}$$

population of level J at temp T = (degeneracy factor) \times (Boltzmann factor)

Note: the assumption that the intrinsic transition probability of a molecule prepared in a state w/ angular momentum J to hop to level J+1 is assumed to be independent of J.

this is true for large J.

$$b) \quad \Delta E = E_{J+1} - E_J = B \underbrace{(J+1)(J+2)}_{J^2+3J+2} - B \underbrace{J(J+1)}_{J^2+J} = \boxed{2(J+1)B}$$

$$c) \quad \text{Set } 0 = \frac{dI_{J \rightarrow J+1}}{dJ} = \left\{ 2 - \underbrace{(2J+1)^2}_{0} \frac{B}{k_B T} \right\} e^{-J(J+1)B/k_B T}$$

Thus

$$\boxed{J_{\max} = \sqrt{\frac{k_B T}{2B}} - \frac{1}{2} \approx \sqrt{\frac{k_B T}{2B}}}$$