

Q1.	6
Q2.	8
Q3.	8
Q4.	6
Q5.	8
Q6.	6
Q7.	8
	<b>50</b>

This is a three-hour test.

Please answer all 7 questions in the spaces provided.

Calculators and the equation sheets provided may be used.

No books or notes are allowed.

Q1. This question refers to the treatment of  $H_2^+$  using the trial wave function  $\psi = c_1 1s_A + c_2 1s_B$ .

a) The trial wave function gives the variational energy  $E' = \frac{c_1^2 H_{AA} + 2c_1 c_2 H_{AB} + c_2^2 H_{AA}}{c_1^2 + 2c_1 c_2 + c_2^2}$

$$\begin{vmatrix} H_{AA} - E & H_{AB} - SE \\ H_{AB} - SE & H_{AA} - E \end{vmatrix} = 0$$

Explain how this result used to obtain the determinantal equation  
by minimizing the  $\frac{\partial E'}{\partial c_1} = 0$   $\frac{\partial E'}{\partial c_2} = 0$   
variational energy

b) What is  $H_{AB}$ ? Why is it important for understanding chemical bonding?

$H_{AB}$  is the exchange integral  $\int 1s_A H 1s_B d\tau = \int 1s_A \hat{H} 1s_B d\tau$

$H_{AB} < 0$   
important for bonding because it stabilizes molecules

[6] c) Show the predicted energies of  $H_2^+$  are  $E_+ = \frac{H_{AA} + H_{AB}}{1+S}$  and  $E_- = \frac{H_{AA} - H_{AB}}{1-S}$ .

from the determinantal equation:

$$(H_{AA} - E)^2 - (H_{AB} - SE)^2 = 0 \Rightarrow H_{AA} - E = \pm (H_{AB} - SE)$$

positive root

$$H_{AA} - E = +(H_{AB} - SE)$$

$$E - SE = H_{AA} - H_{AB}$$

$$E = \frac{H_{AA} - H_{AB}}{1-S}$$

called  $E_-$

negative root

$$H_{AA} - E = -(H_{AB} - SE)$$

$$E + SE = H_{AA} + H_{AB}$$

$$E = \frac{H_{AA} + H_{AB}}{1+S}$$

called  $E_+$

d) Show the wave function  $\psi$  corresponding to energy  $E_+$  is spatially symmetric ( $c_1 = c_2$ ).  
substitute  $E_+$  into the determinant equation

$$(H_{AA} - E_+)c_1 + (H_{AB} - SE_+)c_2 = 0$$

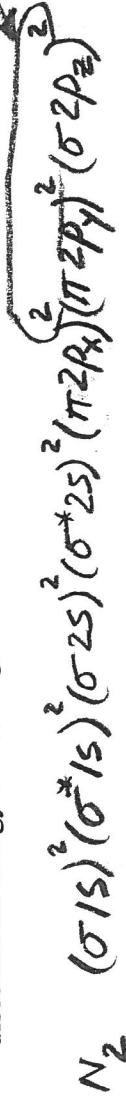
$$\left( H_{AA} - \frac{H_{AA} + H_{AB}}{1+S} \right) c_1 + \left( H_{AB} - S \frac{H_{AA} + H_{AB}}{1+S} \right) c_2 = 0$$

$$\frac{H_{AA}(1+S) - H_{AA} - H_{AB}}{1+S} c_1 + \frac{H_{AB}(1+S) - S H_{AA} - S H_{AB}}{1+S} c_2 = 0$$

$$(S H_{AA} - H_{AB})c_1 - (S H_{AA} - H_{AB})c_2 = 0 \quad c_1 = c_2$$

Q2.

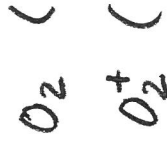
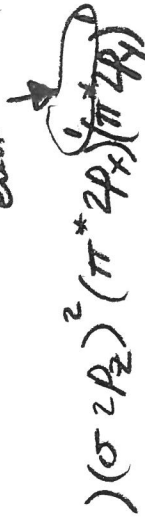
- a) Use MO theory to explain why the dissociation energy of  $N_2$  is greater than that of  $N_2^+$ , but the dissociation energy of  $O_2^+$  is greater than that of  $O_2$ .



bonding electrons



anti-bonding electrons



Bond Orders =

$$N_2 \quad (2+2+2)/2 = 3 \quad | \quad O_2 \quad (2+2+2-2)/2 = 2$$

$$N_2^+ \quad (2+2+1)/2 = 2.5 \quad | \quad O_2^+ \quad (2+2+2-1)/2 = 2.5 \quad (\text{stronger})$$

(weaker)

- b) Electronically-excited molecules usually emit a photon and return to the ground state very rapidly, often in nanoseconds. But excited oxygen molecules in  $^1\Delta$  states can live for hours!

- i) Give two reasons why the conversion of  $^1\Delta$  oxygen to  $^3\Sigma$  ground-state oxygen by the process  $O_2(^1\Delta) \rightarrow O_2(^3\Sigma) + h\nu$  is "forbidden".

selection rules

Singlet  $^1\Delta \rightarrow$  triplet  $^3\Sigma$  forbidden ( $\Delta S = 0$ )

$\Delta(L=2) \rightarrow \Sigma(L=0)$  forbidden ( $\Delta L = \pm 1$ )

- ii) Singlet oxygen can however return to the triplet ground state by the process



Why is this singlet to triplet conversion not "forbidden"?

selection rules  $\Delta S = 0$  and  $\Delta L = \pm 1$  are for electromagnetic spectroscopy transitions, and do not apply to collisions

[8]

- c) Global warming is caused by increasing atmospheric levels of greenhouse gases, such as  $CO_2$ .

- i) Briefly describe the connection between infrared spectroscopy and global warming.

IR radiation from the sun and IR radiation radiated from the surface of the earth is absorbed by  $CO_2$ ,  $H_2O$ ,  $CH_4$ , ... warming the atmosphere

- ii)  $CO_2$  molecules have 4 normal vibration modes, but only 2 IR bands are observed. Why?

the symmetric stretch is IR inactive ( $\nu_1$ )

the two bending modes are degenerate ( $\nu_2 = \nu_3$ )

- iii) Atmospheric levels of  $CO_2$  and  $CH_4$  are about 370 ppm and 1.8 ppm, respectively, but about 25% of global warming is attributed to methane! Suggest why is methane a much more potent greenhouse gas than carbon dioxide.

$CO_2$  (linear) has  $3N-5 = 3(3)-5 = 4$  normal modes

$CH_4$  (nonlinear) has  $3N-6 = 3(5)-6 = 9$  normal modes  
more IR active bands

Q3. a) Huckel  $\pi$ -electron theory is an example of semi-empirical quantum mechanics. What does "semi-empirical" mean in this context?

The wave functions and energies of  $\pi$  electrons are not calculated from  $\hat{H}\psi = E\psi$ . Instead, experimental values of  $\beta$  are used.

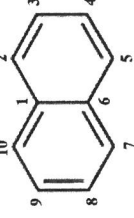
b) In Huckel  $\pi$ -electron theory: i) What is  $\alpha$ ?

$\alpha = \int P_{2i}^* \hat{H} P_{2i} d\tau$  for a  $\pi$  electron on carbon atom  $i$

ii) What is  $\beta$ ?

$\beta = \int P_{2i}^* \hat{H} P_{2i\pm 1} d\tau$  for a  $\pi$  electron on adjacent carbon atoms (exchange integral)

c) Use the provided carbon-atom numbering scheme for naphthalene to write (but not solve!) the Huckel determinantal equation for naphthalene in terms of  $\alpha$ ,  $\beta$  and  $E$ .



$\alpha - E$	$\beta$	0	0	0	$\beta$	0	0	0	0	$\beta$
$\beta$	$\alpha - E$	$\beta$	0	0	0	0	0	0	0	0
0	$\beta$	$\alpha - E$	$\beta$	0	0	0	0	0	0	0
0	0	$\beta$	$\alpha - E$	$\beta$	0	0	0	0	0	0
0	0	0	$\beta$	$\alpha - E$	$\beta$	0	0	0	0	0
$\beta$	0	0	0	$\beta$	$\alpha - E$	$\beta$	0	0	0	0
0	0	0	0	0	$\beta$	$\alpha - E$	$\beta$	0	0	0
0	0	0	0	0	0	0	$\beta$	$\alpha - E$	$\beta$	0
$\beta$	0	0	0	0	0	0	0	0	$\beta$	$\alpha - E$

= 0

[8]

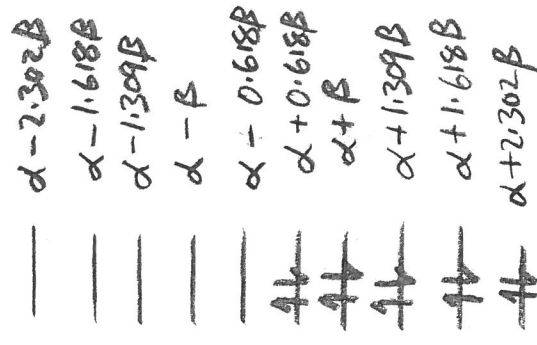
c) Solving the above Huckel determinant equation for naphthalene gives ten  $\pi$ -electron energy levels:

$$\alpha \pm 2.302\beta \quad \alpha \pm 1.618\beta \quad \alpha \pm 1.309\beta \quad \alpha \pm \beta \quad \alpha \pm 0.618\beta$$

Calculate the  $\pi$ -electron energy of naphthalene in terms of  $\alpha$  and  $\beta$ .

$$E_{\pi} = 2(\alpha + 2.302\beta) + 2(\alpha + 1.618\beta) + 2(\alpha + 1.309\beta) + 2(\alpha + \beta) + 2(\alpha + 0.618\beta)$$

$$= 10\alpha + 13.694\beta$$



d) Does delocalization stabilize naphthalene? Justify your answer.

Hint: The energy of a  $\pi$ -electron in ethylene is  $\alpha + \beta$ .

$$\begin{aligned} \text{delocalization energies} &= E_{\pi \text{ naphthalene}} - 5E_{\pi \text{ ethylene}} \\ &= 10\alpha + 13.694\beta - 5(2\alpha + 2\beta) \end{aligned}$$

$$= 3.694\beta$$

$$\beta \approx -75 \text{ kJ mol}^{-1}$$

yes!

Q4. a) Why do chemical bonds form? This question can be answered qualitatively in terms of constructive interference when electron de Broglie wavelengths are similar to bond lengths.

The bond length and ground-state energy of  $H_2^+$  are  $R_0 = 0.106 \text{ nm}$  and  $E = -16.4 \text{ eV}$ .

i) Use the virial theorem  $E = -\langle T \rangle$  to calculate the kinetic energy of the molecule. Almost all of the kinetic energy of  $H_2^+$  is due to the motion of the electron. Why?

$$\langle T \rangle = -E = 16.4 \text{ eV} = 2.63 \times 10^{-18} \text{ J}$$

the protons are  $\sim 2000$  times heavier than electron and "hardly" moving

ii) Calculate the average speed  $v_e$  of the electron in  $H_2^+$ .

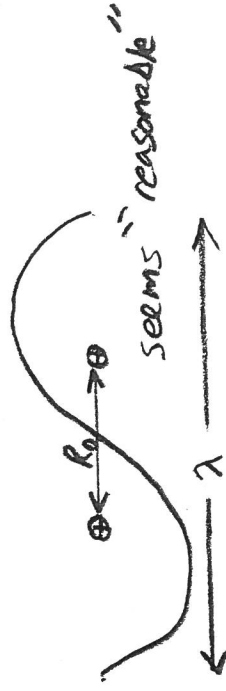
$$\langle T \rangle = 2.63 \times 10^{-18} \text{ J} = \frac{1}{2} m_e v_e^2$$

$$v_e = \sqrt{\frac{2\langle T \rangle}{m_e}} = \sqrt{\frac{2(2.63 \times 10^{-18} \text{ J})}{9.110 \times 10^{-31} \text{ kg}}} = 2.40 \times 10^6 \text{ m s}^{-1}$$

iii) Calculate the de Broglie wavelength  $\lambda = h/m_e v_e$  of the electron. Is  $\lambda$  similar to the  $H_2^+$  bond length? Comment briefly.

$$\lambda = \frac{h}{p_e} = \frac{h}{m_e v_e} = \frac{6.626 \times 10^{-34} \text{ J s}}{(9.110 \times 10^{-31} \text{ kg}) (2.40 \times 10^6 \text{ m s}^{-1})}$$

$$\lambda = 3.03 \times 10^{-10} \text{ m} = \boxed{0.303 \text{ nm}} \approx 3R_0$$



b) For the rotational transition from initial state  $i \rightarrow$  final state  $f$ , use the factor

$$\int_0^{2\pi} e^{i(M_f - M_i)\phi} d\phi = \int_0^{2\pi} e^{i\Delta M \phi} d\phi$$

appearing in the transition dipole moment to derive the spectroscopic selection rule

$$\Delta M = M_f - M_i = 0$$

$$\text{Hint: } e^{iu} = \cos u + i \sin u$$

$$\text{if } \Delta M = 0: \int_0^{2\pi} e^{i\Delta M \phi} d\phi = \int_0^{2\pi} e^{0} d\phi = \int_0^{2\pi} 1 d\phi = 2\pi \neq 0 \quad (\text{transition possible})$$

$$\text{if } \Delta M \neq 0: \int_0^{2\pi} e^{i\Delta M \phi} d\phi = \int_0^{2\pi} \cos(\Delta M \phi) d\phi + i \int_0^{2\pi} \sin(\Delta M \phi) d\phi$$

[6]

$$= \sin(\Delta M \phi) \Big|_0^{2\pi} - i \cos(\Delta M \phi) \Big|_0^{2\pi}$$

$$= \sin(\Delta M 2\pi) - \sin(0) - i [\cos(\Delta M 2\pi) - \cos(0)] = 0 - 0 - i[1 - 1] = 0 \quad (\text{transition forbidden}) = 0$$

f) Use the transition dipole moment for harmonic oscillators

$$(\mu_z)_{n,n'} = \frac{N_n N_{n'}}{\alpha} \left( \frac{d\mu}{dq} \right)_0 \int H_n(\xi) \left[ n H_{n-1}(\xi) + \frac{1}{2} H_{n+1}(\xi) \right] e^{-\xi^2} dq$$

to derive two selection rules for IR spectroscopy.

$(d\mu/dq)_0 \neq 0$  Electric dipole must change as the molecule vibrates

because Hermitic polynomials are orthogonal

$n' = n - 1$  or  $n' = n + 1$  for a possible transition

$$n' - n = \pm 1$$

$$\Delta n = \pm 1$$

Q5. a) Explain why  $\pi$ -electron delocalization stabilizes molecules such as 1,3-butadiene and benzene.

"particle-in-a-box" effect:  
 delocalization places  $\pi$  electrons in a "larger box"  
 with lower energies  $\propto \frac{1}{(\text{box width})^2}$

b) Briefly describe how photo-electron spectroscopy can be used to measure the energies of electrons in atomic and molecular orbitals.

high-energy radiation (usually X radiation)  
 knocks electrons out of atomic or molecular orbitals, causing ionization (e.g.  $He + h\nu \rightarrow He^+ + e^-$ )  
 $h\nu = 15 \text{ eV}$

X-ray photon energy  $h\nu =$  ionization energy of electrons in orbitals

[8] c) At room temperature, 10 to 50 rotational transitions are observed for typical molecules, which substantially complicates the analysis of measured vibrational and electronic spectra. Adiabatic cooling using supersonic jets (mentioned in class) dramatically simplifies rotational spectra, in some case to only one transition! Why?

probability a molecule is in rotational level  $J$   
 is proportional to  $(2J+1) \exp[-BJ(J+1)/kT]$

as  $T \rightarrow 0$  in an adiabatically cooled jet,  $J \rightarrow 0$   
 $P_0 \rightarrow 1, P_1 \rightarrow 0, P_2 \rightarrow 0, P_3 \rightarrow 0, \dots$

all molecules are in the  $J=0$  state,

only the  $J=0$  to  $J=1$  transition occurs

d) Give two reasons why the trial wave function  $\psi = 1s_A(1)1s_B(2)$  for  $H_2$  is unacceptable.

①  $\psi(1,2) = 1s_A(1)1s_B(2) \neq \psi(2,1) = 1s_B(2)1s_A(1)$

not asymmetric with respect to electron interchange

② can't say electron 1 is in  $1s_A(1)$  orbital and electron 2 is in  $1s_B(2)$  orbital (electrons are indistinguishable) (3 no spin factor)

e) The Schrodinger equation  $\hat{H}\psi = E\psi$  contains no energy terms for electron spin, but we used the Schrodinger equation to derive singlet and triplet states of  $H_2$  with different energies! How is this possible?

Spatially-symmetric  $\psi_+$  ( $c_1 = c_2$ ) is multiplied by

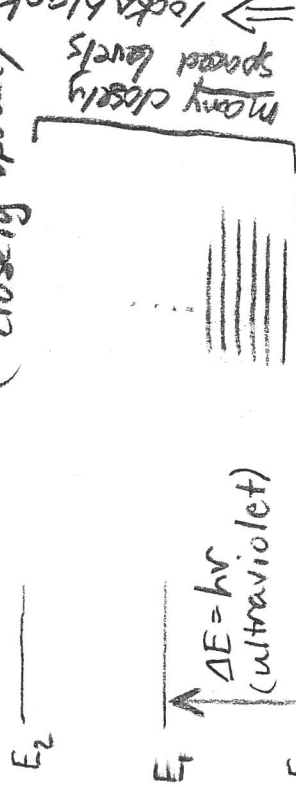
an antisymmetric paired-electron spin function (bonding) such as  $[\alpha(1)\beta(2) - \alpha(2)\beta(1)]$  to give the lower energy (bonding) wave function

spatially-unsymmetric  $\psi_-$  ( $c_1 = -c_2$ ) multiplied by

symmetric spin function [e.g.  $\alpha(1)\alpha(2)$ ] to give the higher energy

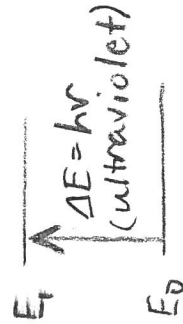
f) Explain why  $\pi$  to  $\pi^*$  transitions shift to lower frequencies and become more numerous for longer-chain conjugated molecules. Also, suggest why graphite appears black to the eye.

short chain: long chain:  
 (colorless) (energy levels closely spaced)



long-chain molecules have smaller energy differences between  $\pi$ -electron energy levels

shifts  $\Delta E$  and  $h\nu$  to lower frequencies (visible and IR)



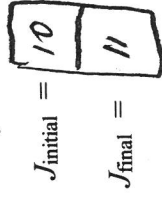
Q6. This question refers to the microwave spectrum of  $^{12}\text{C}^{16}\text{O}$ . Data:

equilibrium bond length  $r_{\text{eq}} = 0.1128 \text{ nm}$   
force constant  $k = 1870 \text{ N m}^{-1}$

reduced mass  $\mu = 1.139 \times 10^{-26} \text{ kg}$   
fundamental frequency  $\nu_e = 2170 \text{ cm}^{-1}$

a) The diagram shows a microwave absorption spectrum measured for  $^{12}\text{C}^{16}\text{O}$ .

Give the initial and final  $J$  values for the transition indicated by the arrow.



$$\Delta J = +1$$

(absorption)

b) The first four frequencies in the microwave spectrum of  $^{12}\text{C}^{16}\text{O}$  are 3.8454, 7.6906, 11.5355, and 15.3799  $\text{cm}^{-1}$ .

Use this data to show: i) the rigid rotor approximation is very accurate

$$\tilde{\nu}_2 - \tilde{\nu}_1 = 3.8452 \text{ cm}^{-1} \quad \tilde{\nu}_3 - \tilde{\nu}_2 = 3.8449 \text{ cm}^{-1} \quad \tilde{\nu}_4 - \tilde{\nu}_3 = 3.8444 \text{ cm}^{-1}$$

line spacing changes by only 0.02%  
 $^{12}\text{C}^{16}\text{O}$  is very nearly rigid

[6] ii) the bond length of  $^{12}\text{C}^{16}\text{O}$  increases slightly with increasing rotational energy.

$$2B = \frac{h^2}{8\pi^2 I}$$

the spacing of rotational lines is  $2B$  as the rotational energy increases, the data show the spacing decreases by 0.02%

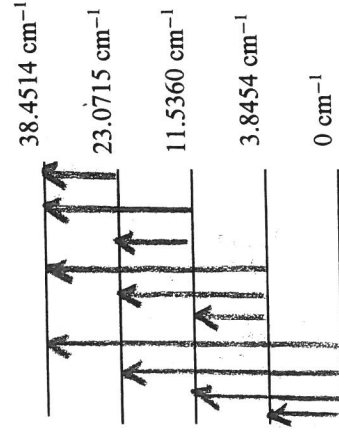
this means the moment of inertia  $I$  is increasing

$$I = \mu r^2 = \left( \frac{m_e m_o}{m_e + m_o} \right) r^2 \quad \text{which means } r \text{ is increasing}$$

constant (centrifugal stretching)

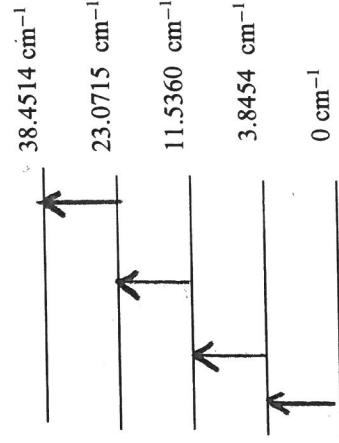
c) The first five rotational energy levels of  $^{12}\text{C}^{16}\text{O}$  are sketched below (not to scale). To illustrate the importance of spectroscopic selection rules, use appropriate arrows to indicate the absorption transitions between these energy levels assuming

i) no selection rules apply



$\Delta J$  unrestricted

ii) rotational selection rules apply

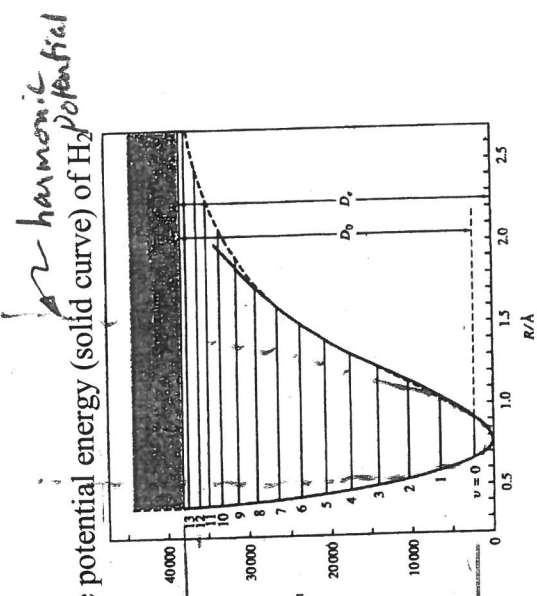


$\Delta J = +1$  (absorption)

d) Why is microwave spectroscopy not useful for determining the structure (linear or triangular) of  $\text{H}_3^+$ ?

$+1/3$  (linear or triangular) does not have an electric dipole moment ( $\vec{\mu} = 0$ )  
 $\Rightarrow$  microwave inactive

Q7. Use the vibrational energy levels (horizontal lines) and the potential energy (solid curve) of H<sub>2</sub> plotted below to answer this question.



a) Give the dissociation energy of H<sub>2</sub> in units of eV.

dissociation energy = D<sub>0</sub>  
 $\tilde{D}_0 \approx 36,000 \text{ cm}^{-1}$  (read from graph)

$$\tilde{D}_0 = \frac{D_0}{hc} \quad D_0 = hc\tilde{D}_0$$

$$D_0 = (6.626 \times 10^{-34} \text{ Js})(2.998 \times 10^{10} \text{ cm}^{-1} \text{ s})(36000 \text{ cm}^{-1}) = 7.15 \times 10^{-19} \text{ J} = 4.46 \text{ eV}$$

b) The vibrational energy-level spacing for a harmonic are equally spaced, but the diagram shows H<sub>2</sub> vibrational energy levels get closer as n increases. Explain.

the potential energy curve widens more than the harmonic potential ( $\frac{1}{2}k(r-r_0)^2$ ), causing the energy spacing to decrease (particle-in-a-box effect, again!).

c) The Morse potential (dashed curve) gives the vibrational energy levels

$$E_n = h\nu_e(n + \frac{1}{2}) - x_e h\nu_e(n + \frac{1}{2})^2 \quad n = 0, 1, 2, 3, \dots$$

i) What are  $\nu_e$  and  $x_e$ ?

$\nu_e$  fundamental vibration frequency  
 $x_e$  anharmonicity constant

ii) Show the vibrational energy difference  $E_{n+1} - E_n$  using the Morse potential is

$$E_{n+1} - E_n = h\nu_e[1 - 2x_e(n + 1)]$$

$$\begin{aligned} E_{n+1} - E_n &= h\nu_e(n + \frac{1}{2}) - x_e h\nu_e(n + \frac{1}{2})^2 - h\nu_e(n + \frac{1}{2})^2 + x_e h\nu_e(n + \frac{1}{2})^2 \\ &= h\nu_e + x_e h\nu_e[(n + \frac{1}{2})^2 - (n + 1 + \frac{1}{2})^2] \\ &= h\nu_e + x_e h\nu_e[n^2 + n + \frac{1}{4} - n^2 - 2\frac{3}{2}n - \frac{9}{4}] \\ &= h\nu_e + x_e h\nu_e[-2n - 2] = h\nu_e - 2x_e h\nu_e(n + 1) \end{aligned}$$

iii) Why does  $E_{n+1} - E_n$  drop to zero in the dissociation limit H<sub>2</sub> → 2H?

→ "box" is infinitely wide  
 $\Delta E \rightarrow 0$  as  $\frac{1}{L^2} \rightarrow 0$

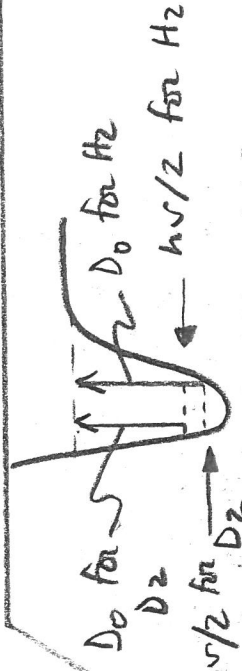
d)  $x_e = 0.02682$  for H<sub>2</sub>. Use the Morse potential to estimate the maximum vibrational quantum number n before H<sub>2</sub> "shakes itself apart". Does this value of n agree with experiment? Explain.

$$0 = h\nu_e[1 - 2x_e(n_{\text{max}} + 1)] \quad 0 = 1 - 2x_e(n_{\text{max}} + 1)$$

$$n_{\text{max}} = \frac{1}{2x_e} - 1$$

$$= 17.6$$

$$\approx 18$$



e) Would you expect H<sub>2</sub> and D<sub>2</sub> to have the same values of D<sub>e</sub> and D<sub>0</sub>? Discuss briefly.

→ same D<sub>e</sub> extra neutrons (zero electric charge) has almost no effect on the electronic structure and therefore no effect on D<sub>e</sub>

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Smaller D<sub>0</sub> for H<sub>2</sub> the extra nuclear mass for D<sub>2</sub> reduces the zero-point vibrational energy  $\frac{1}{2}h\sqrt{\frac{k}{m}}$