

NAME:

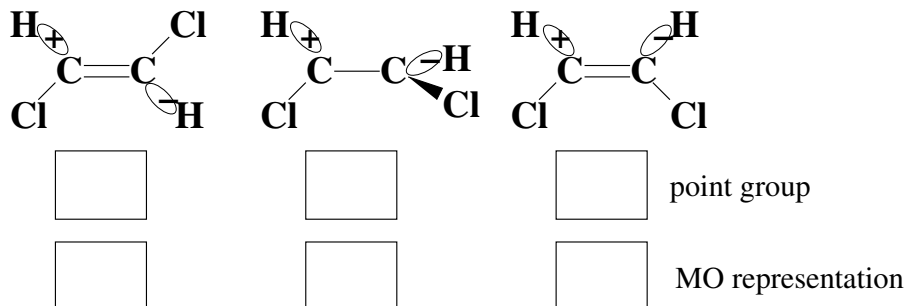
Instructions:

1. Keep this exam closed until instructed to begin. Please write your name on this page but not on any other page.
2. Please silence any noisy electronic devices you have.
3. Attached sheet(s) provide potentially useful constants and equations. You may detach these from the exam if you prefer.
4. To receive full credit for your work, please
 - (a) show all your work, using the back of this sheet if necessary,
 - (b) specify the correct units, if any, for your final answers,
 - (c) stop writing and close your exam immediately when time is called.

Other notes:

- **Your 4 best scores of the 5 problems will constitute your total score.**
- Partial credit is available for all problems, so try each problem and do not erase any of your work.
- Each question is worth 25 points, but they are not intended to be equally easy.

1. One of the symmetry molecular orbitals for the C—H bonds in dichloroethene is drawn below as the molecule isomerizes from *trans* to *cis*. Fill in the blanks below for the point group of the molecule and the representation of the orbital at these three geometries. Let the two carbons lie along the x axis in each case.

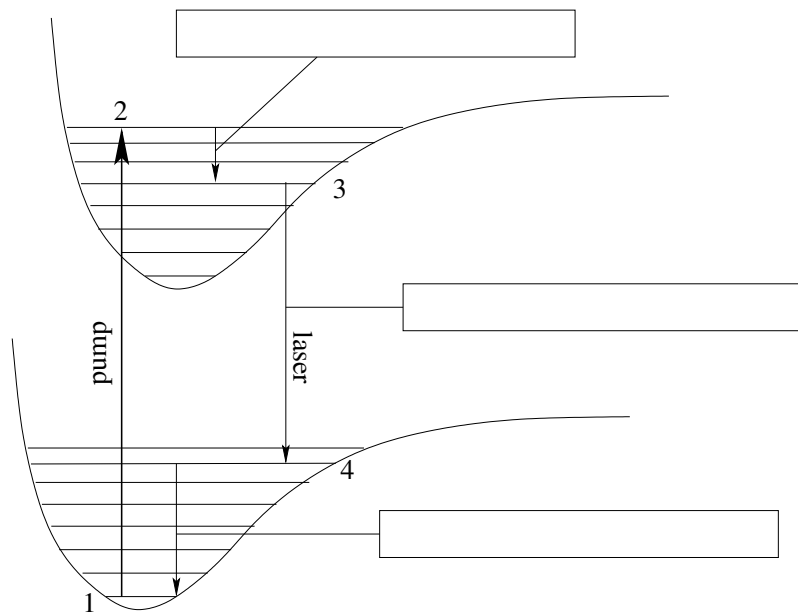


2. For the molecular ion Be_2^+ :

(a) write the MO configuration and term symbol for the ground electronic state X ;

(b) form an excited state A by promoting the highest energy electron to the lowest energy unoccupied MO, and determine if the transition $X \rightarrow A$ is allowed or forbidden by electric dipole selection rules.

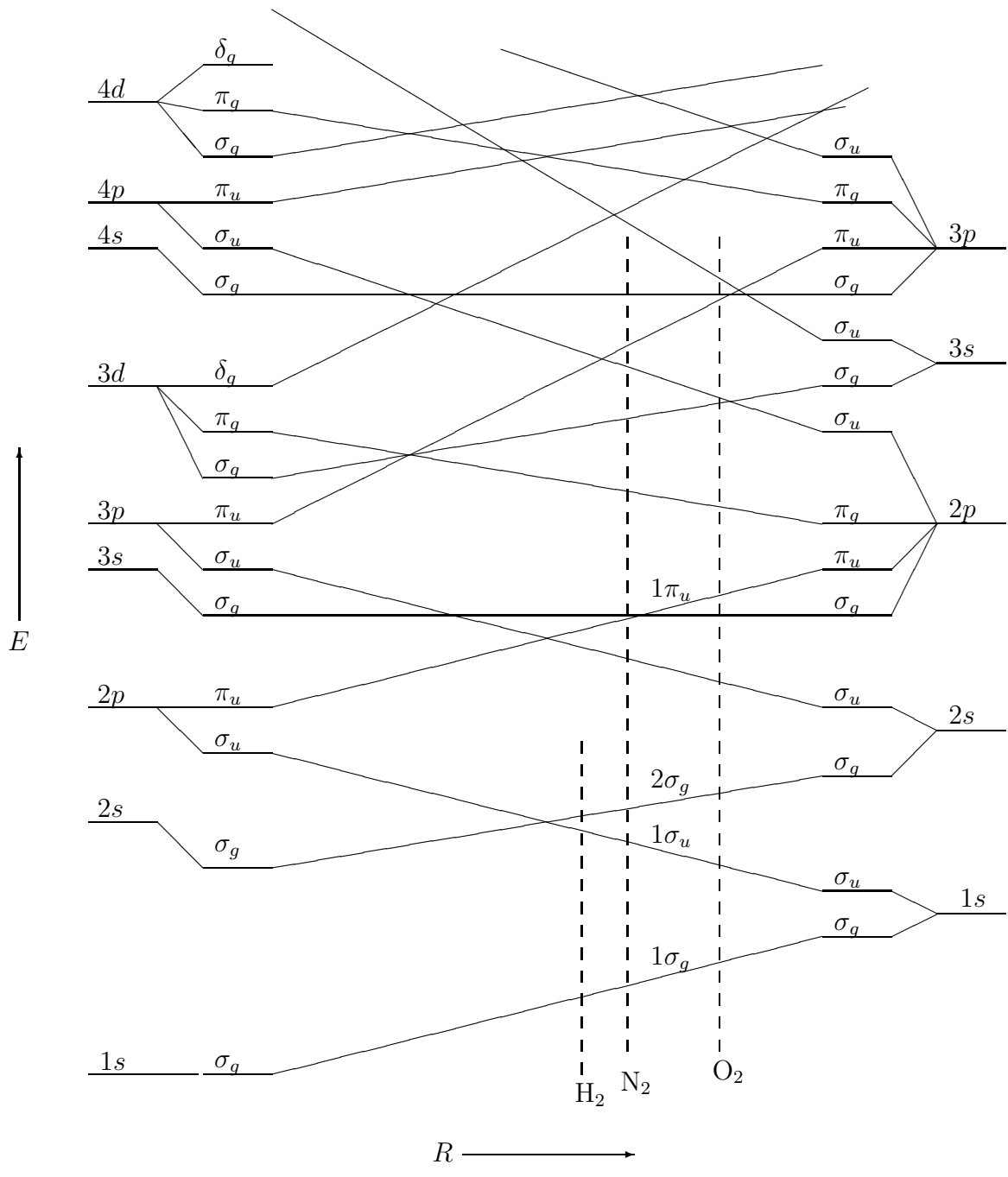
3. In a typical liquid dye laser, a dissolved compound is excited from a low energy state 1 to an upper state 2 by an energy source called the “pump.” Some energy is lost to reach state 3, and the laser radiation is released by the allowed transition 3 → 4. Identify any energetic process (photoionization, level-crossing, etc.) that could be responsible for each of the three energy-loss steps 2 → 3, 3 → 4, and 4 → 1, in the boxes provided below.



4. Write an expression that would determine the tunnelling probability of the $v = 1$ harmonic oscillator wavefunction, *i.e.*, the probability density that lies in the tunnelling region.

5. Using your best judgement, put the following in order of **increasing value** of the vibrational constant ω_e :

(a) $^{31}\text{P}^{34}\text{S}$ (b) $^{31}\text{P}_2^+$ (c) $^{31}\text{P}^{14}\text{N}$ (d) $^{31}\text{P}^{32}\text{S}$ (e) $^{31}\text{P}_2$



v	A_v	$H_v(y)$	nodes
0	$\left(\frac{k\mu}{\hbar^2}\right)^{1/8} \left(\frac{1}{\sqrt{\pi}}\right)^{1/2}$	1	0
1	$\left(\frac{k\mu}{\hbar^2}\right)^{1/8} \left(\frac{1}{2\sqrt{\pi}}\right)^{1/2}$	$2y$	1 : $y = 0$
2	$\left(\frac{k\mu}{\hbar^2}\right)^{1/8} \left(\frac{1}{8\sqrt{\pi}}\right)^{1/2}$	$4y^2 - 2$	2 : $y = \pm 1.414$
3	$\left(\frac{k\mu}{\hbar^2}\right)^{1/8} \left(\frac{1}{48\sqrt{\pi}}\right)^{1/2}$	$8y^3 - 12y$	3 : $y = 0, \pm 1.225$
4	$\left(\frac{k\mu}{\hbar^2}\right)^{1/8} \left(\frac{1}{384\sqrt{\pi}}\right)^{1/2}$	$16y^4 - 48y^2 + 12$	4 : $y = \pm 0.525, \pm 1.651$
5	$\left(\frac{k\mu}{\hbar^2}\right)^{1/8} \left(\frac{1}{3840\sqrt{\pi}}\right)^{1/2}$	$32y^5 - 160y^3 + 120y$	5 : $y = 0, \pm 0.959, \pm 2.020$
$y H_v(y) = v H_{v-1}(y) + \frac{1}{2} H_{v+1}(y)$		$y \eta_v(y) = A_v$	$v \frac{\eta_{v-1}(y)}{A_{v-1}} + \frac{1}{2} \frac{\eta_{v+1}(y)}{A_{v+1}}$
$\frac{dH_v(y)}{dy} = v H_{v-1}(y) - \frac{1}{2} H_{v+1}(y)$		$\frac{d\eta_v(y)}{dy} = A_v$	$v \frac{\eta_{v-1}(y)}{A_{v-1}} - \frac{1}{2} \frac{\eta_{v+1}(y)}{A_{v+1}}$

Selected vibrational and rotational constants.

Molecule	μ (amu)	R_e (Å)	B_e (cm ⁻¹)	α_e (cm ⁻¹)	D (10 ⁻⁶ cm ⁻¹)	ω_e (cm ⁻¹)
¹ H ¹ H	0.50	0.742	60.8536	3.0622		46660
¹ H ² D	0.67	0.742	45.6378	1.9500		3811.92
² D ² D	1.01	0.742	30.442	1.0623		3118.46
¹ H ¹⁹ F	0.96	0.917	20.9557	0.798	2150	4138.32
¹ H ³⁵ Cl	0.98	1.275	10.5934	0.3702	532	2990.95
¹ H ⁷⁹ Br	1.00	1.414	8.3511	0.226	372	2649.67
¹ H ¹²⁷ I	1.00	1.609	3.2535	0.0608	526	2309.60
² D ¹⁹ F	1.82	0.917	11.0000	0.2907	585	2998.19
¹² C ¹⁶ O	6.86	1.128	1.9313	1.7507	6	2169.82
¹⁴ N ¹⁴ N	7.00	1.098	1.9987	0.0171	6	2358.07
¹⁴ N ¹⁶ O ⁺	7.47	1.063	1.9982	0.0190		2377.48
¹⁴ N ¹⁶ O	7.47	1.151	1.7043	0.0173	-37	1904.41
¹⁴ N ¹⁶ O ⁻	7.47	1.286	1.427			1372
¹⁶ O ¹⁶ O	8.00	1.207	1.4457	0.0158	5	1580.36
¹⁹ F ¹⁹ F	9.50	1.418	0.8828			891.2
³⁵ Cl ³⁵ Cl	17.48	1.988	0.2441	0.0017	0.2	560.50
⁷⁹ Br ⁷⁹ Br	39.46	2.67	0.0821	0.0003	0.02	325.29
¹²⁷ I ⁷⁹ Br	48.66	2.470	0.0559	0.0002	0.008	268.71
¹²⁷ I ¹²⁷ I	63.45	2.664	0.0374	0.0001	-0.005	214.52
²³ Na ²³ Na	11.49	3.077	0.1548	0.0009	0.7	159.13
¹³³ Cs ¹³³ Cs	66.45	4.47	0.0127	0.00003	0.005	42.02

vibration $\eta_v(R) = A_v H_v(y) e^{-(R-R_e)^2/(2c^2)}, \quad c = \left(\frac{\hbar^2}{k\mu}\right)^{1/4}$

$$E_{\text{vib}} = \omega_e \left(v + \frac{1}{2}\right) - \omega_e x_e \left(v + \frac{1}{2}\right)^2 + \dots$$

$$\omega_e = \hbar \sqrt{\frac{k}{\mu}}$$

Morse potential $E_{\text{elec}}(R) = D_e \left\{ \left[1 - e^{-\beta(R-R_e)} \right]^2 - 1 \right\}$