Chemistry 410A **Exam 4** **Spring 2016**

NAME:

Instructions:

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

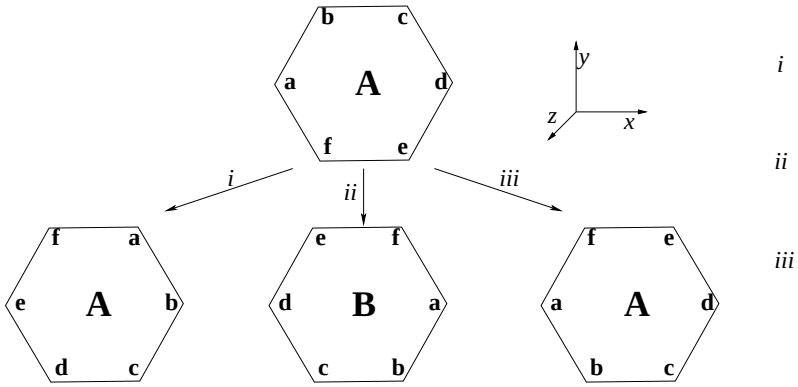
Other notes:

- **Problem 1 (covering all of page 3) of the exam is worth 40 points.** Partial credit for these problems is not necessarily available.
- **Your 2 best scores of the 3 remaining problems will count towards the other 60 points.** Partial credit is available for these problems, so try each problem and do not erase any of your work.

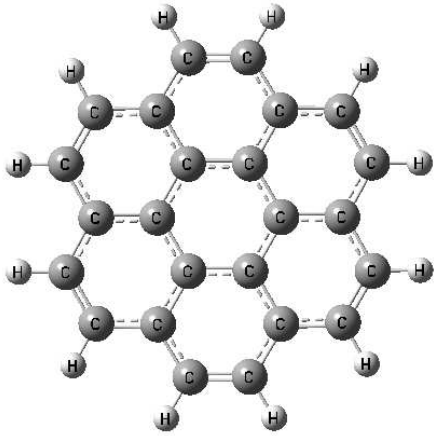
1. **40 points.**

(a) **10 points.** In the space below, sketch the curve for the effective potential energy U_{eff} seen by the nuclei in a diatomic molecule as a function of R.

(b) **10 points.** What single symmetry operation would accomplish each of the transformations shown below?



(c) **20 points.** List all the symmetry elements and find the point group of the molecule coronene, sketched below. Label your axes and planes as needed.



2. Two functions $f(x)$ and $g(x)$ are orthogonal if $\int f(x)g(x)\,dx = 0$ over all space.

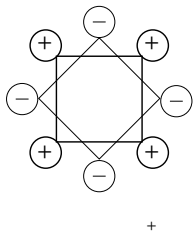
   (a) Show whether or not the ψ_+ and ψ_- orbitals of H_2^+ are orthogonal.

   (b) Show whether or not the ψ_+ molecular orbital of H_2^+ and the $1s_A$ atomic orbital of hydrogen are orthogonal.

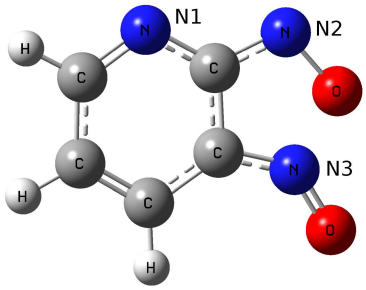
3. (a) What point group contains the operators listed below? ($\hat{\sigma}_d$ is a kind of $\hat{\sigma}_v$.)

$\hat{E}$	$2\hat{C}_4$	$\hat{C}_2$	$4\hat{\sigma}_d$	$4\hat{C}_2'$	$4\hat{S}_8$

   (b) The non-degenerate orbital sketched below belongs to this point group. The $\oplus$ phase parts of the orbital lie in a plane above the plane of the four $\ominus$ parts. Write the characters for this representation under each operator listed above. (Don't worry about naming the representation.)



4. The following shielding parameters are calculated for the nitrogen nuclei in the nitropyridine shown and for the ammonia reference:



N1: -51.05 N2: -134.63 N3: -125.14 NH_3: 269.06
(The negative values indicate that there is some paramagnetic character.)

(a) Predict the frequency in MHz of the highest energy transition in the ^{14}N NMR spectrum at $B = 14.0\,\mathrm{T}$.

(b) Briefly state one or two **advantages** of each N-atom isotope in NMR spectroscopy below.

^{14}**N**	^{14}**N**

(c) In the area below, sketch the ^{15}N NMR spectrum as a function of δ. Give approximate numerical values for the horizontal axis.

Fundamental Constants

Avogadro's number	$\mathcal{N}_A$	$6.0221367 \cdot 10^{23}$ mol^{-1}
Bohr radius	$a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2}$	$5.29177249 \cdot 10^{-11}$ m
Boltzmann constant	k_B	$1.380658 \cdot 10^{-23}$ J K^{-1}
electron rest mass	m_e	$9.1093897 \cdot 10^{-31}$ kg
fundamental charge	e	$1.6021773 \cdot 10^{-19}$ C
permittivity factor	$4\pi\epsilon_0$	$1.113 \cdot 10^{-10}$ C^2 J^{-1} m^{-1}
gas constant	R	8.314510 J K^{-1} mol^{-1}
	R	0.08314510 L bar K^{-1} mol^{-1}
	R	0.08206 L atm K^{-1} mol^{-1}
hartree	$E_\mathrm{h} = \frac{m_e e^4}{(4\pi\epsilon_0)^2\hbar^2}$	$4.35980 \cdot 10^{-18}$ J
Planck's constant	h	$6.6260755 \cdot 10^{-34}$ J s
	$\hbar$	$1.05457266 \cdot 10^{-34}$ J s
proton rest mass	m_p	$1.6726231 \cdot 10^{-27}$ kg
neutron rest mass	m_n	$1.6749286 \cdot 10^{-27}$ kg
speed of light	c	$2.99792458 \cdot 10^{8}$ m s^{-1}

Unit Conversions

	K	cm^{-1}	kJ mol^{-1}	kcal mol^{-1}	erg	kJ
kHz =	$4.799 \cdot 10^{-8}$	$3.336 \cdot 10^{-8}$	$3.990 \cdot 10^{-10}$	$9.537 \cdot 10^{-11}$	$6.626 \cdot 10^{-24}$	$6.626 \cdot 10^{-34}$
MHz =	$4.799 \cdot 10^{-5}$	$3.336 \cdot 10^{-5}$	$3.990 \cdot 10^{-7}$	$9.537 \cdot 10^{-8}$	$6.626 \cdot 10^{-21}$	$6.626 \cdot 10^{-31}$
GHz =	$4.799 \cdot 10^{-2}$	$3.336 \cdot 10^{-2}$	$3.990 \cdot 10^{-4}$	$9.537 \cdot 10^{-5}$	$6.626 \cdot 10^{-18}$	$6.626 \cdot 10^{-28}$
K =	1	0.6950	$8.314 \cdot 10^{-3}$	$1.987 \cdot 10^{-3}$	$1.381 \cdot 10^{-16}$	$1.381 \cdot 10^{-26}$
cm^{-1} =	1.4388	1	$1.196 \cdot 10^{-2}$	$2.859 \cdot 10^{-3}$	$1.986 \cdot 10^{-16}$	$1.986 \cdot 10^{-26}$
kJ mol^{-1} =	$1.203 \cdot 10^{2}$	83.59	1	0.2390	$1.661 \cdot 10^{-14}$	$1.661 \cdot 10^{-24}$
kcal mol^{-1} =	$5.032 \cdot 10^{2}$	$3.498 \cdot 10^{2}$	4.184	1	$6.948 \cdot 10^{-14}$	$6.948 \cdot 10^{-24}$
eV =	$1.160 \cdot 10^{4}$	$8.066 \cdot 10^{3}$	96.49	23.06	$1.602 \cdot 10^{-12}$	$1.602 \cdot 10^{-22}$
hartree =	$3.158 \cdot 10^{5}$	$2.195 \cdot 10^{5}$	$2.625 \cdot 10^{3}$	$6.275 \cdot 10^{2}$	$4.360 \cdot 10^{-11}$	$4.360 \cdot 10^{-21}$
erg =	$7.243 \cdot 10^{15}$	$5.034 \cdot 10^{15}$	$6.022 \cdot 10^{13}$	$1.439 \cdot 10^{13}$	1	10^{-10}
J =	$7.243 \cdot 10^{22}$	$5.034 \cdot 10^{22}$	$6.022 \cdot 10^{20}$	$1.439 \cdot 10^{20}$	10^{7}	10^{-3}
dm^3 bar =	$7.243 \cdot 10^{24}$	$5.034 \cdot 10^{24}$	$6.022 \cdot 10^{22}$	$1.439 \cdot 10^{22}$	$1.000 \cdot 10^{9}$	0.1000
kJ =	$7.243 \cdot 10^{25}$	$5.034 \cdot 10^{25}$	$6.022 \cdot 10^{23}$	$1.439 \cdot 10^{23}$	10^{10}	1

distance	1 Å =	10^{-10} m	
mass	1 amu =	$1.66054 \cdot 10^{-27}$ kg	
energy	1 J =	1 kg m^2 s^{-2}	$= 10^7$ erg
force	1 N =	1 kg m s^{-2}	$= 10^5$ dyn
electrostatic charge	1 C =	1 A s	$= 2.9979 \cdot 10^9$ esu
	1 D =	$3.3357 \cdot 10^{-30}$ C m	$= 1 \cdot 10^{-18}$ esu cm
magnetic field strength	1 T =	1 kg s^{-2} A^{-1}	$= 10^4$ gauss
pressure	1 Pa =	1 N m^{-2}	= 1 kg m^{-1} s^{-2}
	1 bar =	10^5 Pa	= 0.98692 atm

H_2^+ MO wavefunctions: $\psi_\pm(r,\theta,R) = C_\pm(R)(1s_\mathrm{A} \pm 1s_\mathrm{B})$

NMR energy: $E_{\mathrm{mag},I} = -g_I \mu_N m_I B_\mathrm{local}$

NMR transition energy: $\Delta E_{\mathrm{mag},I} = |g_I \mu_N B_0 (1-\sigma)|$

chemical shift: $\delta = \dfrac{\sigma_0 - \sigma}{1 - \sigma_0}$

C_2	$\hat{E}$	$\hat{C}_2$	Functions
$A(a)$	1	1	$z; x^2, y^2, z^2, xy; R_z$
$B(b)$	1	-1	$x, y; yz, xz; R_x, R_y$

C_{2h}	$\hat{E}$	$\hat{C}_2$	$\hat{I}$	$\hat{\sigma}_h$	Functions
$A_g(a_g)$	1	1	1	1	$x^2, y^2, z^2, xy; R_z$
$B_g(b_g)$	1	-1	1	-1	$xz, yz; R_x, R_y$
$A_u(a_u)$	1	1	-1	-1	z
$B_u(b_u)$	1	-1	-1	1	x, y

C_{2v}	$\hat{E}$	$\hat{C}_2(z)$	$\hat{\sigma}_v(xz)$	$\hat{\sigma}'_v(yz)$	Functions
$A_1(a_1)$	1	1	1	1	$z; x^2, y^2, z^2$
$A_2(a_2)$	1	1	-1	-1	$xy; R_z$
$B_1(b_1)$	1	-1	1	-1	$x; xz; R_y$
$B_2(b_2)$	1	-1	-1	1	$y; yz; R_x$

D_2	$\hat{E}$	$\hat{C}_2(z)$	$\hat{C}_2(y)$	$\hat{C}_2(x)$	Functions
$A(a)$	1	1	1	1	x^2, y^2, z^2
$B_1(b_1)$	1	1	-1	-1	$z; xy; R_z$
$B_2(b_2)$	1	-1	1	-1	$y; xz; R_y$
$B_3(b_3)$	1	-1	-1	1	$x; yz; R_x$

D_{2d}	$\hat{E}$	$2\hat{S}_4$	$\hat{C}_2$	$2\hat{C}'_2$	$2\hat{\sigma}_d$	Functions
$A_1(a_1)$	1	1	1	1	1	$x^2 + y^2, z^2$
$A_2(a_2)$	1	1	1	-1	-1	R_z
$B_1(b_1)$	1	-1	1	1	-1	$x^2 - y^2$
$B_2(b_2)$	1	-1	1	-1	1	$z; xy$
$E(e)$	2	0	-2	0	0	$(x, y); (xz, yz); (R_x, R_y)$

D_{2h}	$\hat{E}$	$\hat{C}_2(z)$	$\hat{C}_2(y)$	$\hat{C}_2(x)$	$\hat{I}$	$\hat{\sigma}(xy)$	$\hat{\sigma}(xz)$	$\hat{\sigma}(yz)$	Functions
$A_g(a_g)$	1	1	1	1	1	1	1	1	x^2, y^2, z^2
$B_{1g}(b_{1g})$	1	1	-1	-1	1	1	-1	-1	$xy; R_z$
$B_{2g}(b_{2g})$	1	-1	1	-1	1	-1	1	-1	$xz; R_y$
$B_{3g}(b_{3g})$	1	-1	-1	1	1	-1	-1	1	$yz; R_x$
$A_u(a_u)$	1	1	1	1	-1	-1	-1	-1	
$B_{1u}(b_{1u})$	1	1	-1	-1	-1	-1	1	1	z
$B_{2u}(b_{2u})$	1	-1	1	-1	-1	1	-1	1	y
$B_{3u}(b_{3u})$	1	-1	-1	1	-1	1	1	-1	x