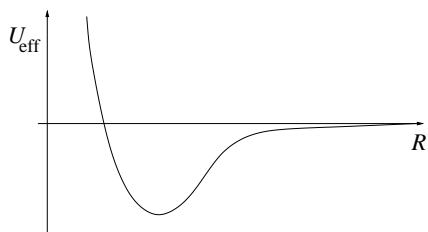
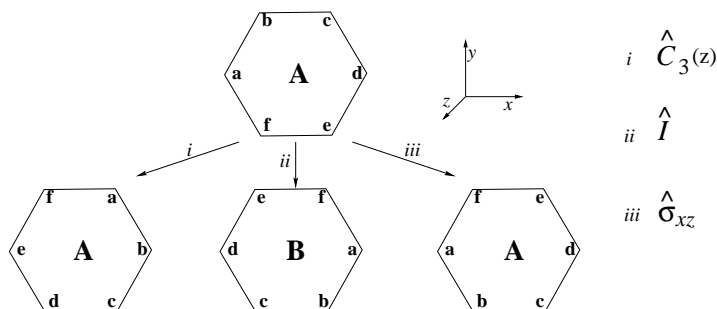


## 1. 40 points.

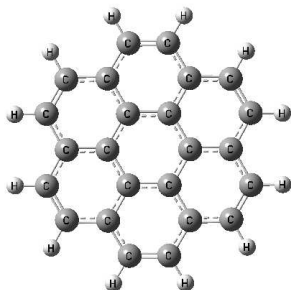
- (a) In the space below, sketch the curve for the effective potential energy  $U_{\text{eff}}$  seen by the nuclei in a diatomic molecule as a function of  $R$ .



- (b) What single symmetry operation would accomplish each of the transformations shown below?



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



**Solution:** The molecule has a principal  $\hat{C}_6$  axis perpendicular to the page, a horizontal mirror reflection  $\hat{\sigma}_h$ , 6 vertical mirror plane reflections  $\hat{\sigma}_v$ , 6  $\hat{C}_2$  axes perpendicular to the principal axis, inversion, and the  $\hat{S}_6$  improper rotations about the principal axis. The point group is  $D_{6h}$ .

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  $\psi_+$  and  $\psi_-$  orbitals of  $\text{H}_2^+$  are orthogonal. **Solution:** We can ignore the normalization constant. If the integral vanishes, it will do so whether

or not we multiply it by the right constant. But let's assume that the  $1s$  orbitals are already normalized.

$$\int (1s_A + 1s_B)(1s_A - 1s_B) d\tau = \int 1s_A^2 d\tau + \int 1s_A 1s_B d\tau - \int 1s_A 1s_B d\tau - \int 1s_B^2 d\tau = 1 - 1 = 0.$$

They are orthogonal.

- (b) Show whether or not the  $\psi_+$  molecular orbital of  $H_2^+$  and the  $1s_A$  atomic orbital of hydrogen are orthogonal. **Solution:**

$$\int (1s_A + 1s_B) 1s_A d\tau = \int 1s_A^2 d\tau + \int 1s_A 1s_B d\tau = 1 - \int 1s_A 1s_B d\tau > 0.$$

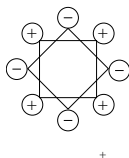
We know that  $0 < \int 1s_A 1s_B d\tau < 1$  because the  $1s$  orbitals are positive everywhere (so the integral cannot be negative) and the integral reaches its maximum value of one only in the limit that nuclei A and B are on top of one another (so that  $1s_A = 1s_B$ ).

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

$\hat{E}$	$2\hat{C}_4$	$\hat{C}_2$	$4\hat{\sigma}_d$	$4\hat{C}'_2$	$4\hat{S}_8$
1	1	1	1	-1	-1

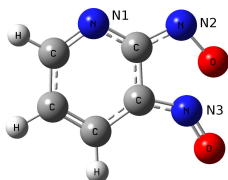
**Solution:** There is a principal axis with  $n = 4$  plus  $n$  additional  $\hat{C}'_2$  axes, so this is one of the  $D$  groups. There is no  $\hat{\sigma}_h$ , so it is not  $D_{4h}$ . There are vertical mirror planes, so that makes this  $D_{4d}$ .

- (b) The orbital sketched below belongs to this point group. Write the characters for this representation under each operator listed above.



**Solution:** Shown above. The orbital has all the same phase each side of the  $xy$  plane, and opposite phases on opposite sides of the  $xy$  plane. Only the  $\hat{C}'_2$  and  $\hat{S}_8$  operators will reflect through the  $xy$  plane, so only those characters are negative. This is the representation  $b_2$  in  $D_{4d}$ .

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<sub>3</sub>:  $269.06$   
 (The negative values indicate that there is some paramagnetic character.)

- (a) Predict the frequency in MHz of the highest energy transition in the <sup>14</sup>N NMR spectrum of nitropyridine at  $B = 14.0$  T. **Solution:** The highest frequency transition will be the one with the least shielding (here the most negative value of  $\sigma$ , N2), but to the tenth of a MHz it doesn't matter which one you use:

$$\begin{aligned} \Delta E_{\text{mag},I} &= |g_I \mu_N B_0 (1 - \sigma)| \\ &= |(0.404)(5.05 \cdot 10^{-27} \text{ J T}^{-1})^{-1} (14.0 \text{ T})(6.626 \cdot 10^{-28} \text{ J/MHz}) [1 - (-125.14 \cdot 10^{-6})]| \\ &= \boxed{43.1 \text{ MHz.}} \end{aligned}$$

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

<sup>14</sup> N	<sup>15</sup> N
much more abundant	spin 1/2 spectrum easier to analyze than spin 1
greater magnitude $g_I$ means better resolution	

- (c) In the area below, sketch the <sup>15</sup>N NMR spectrum as a function of  $\delta$ . Give approximate numerical values for the horizontal axis. **Solution:** The chemical shift  $\delta \approx \sigma_0 - \sigma$ , so:  $\delta = 320.1$  for N1,  $403.69$  for N2,  $394.19$  for N3, and  $0$  for NH<sub>3</sub>:

