

Part I

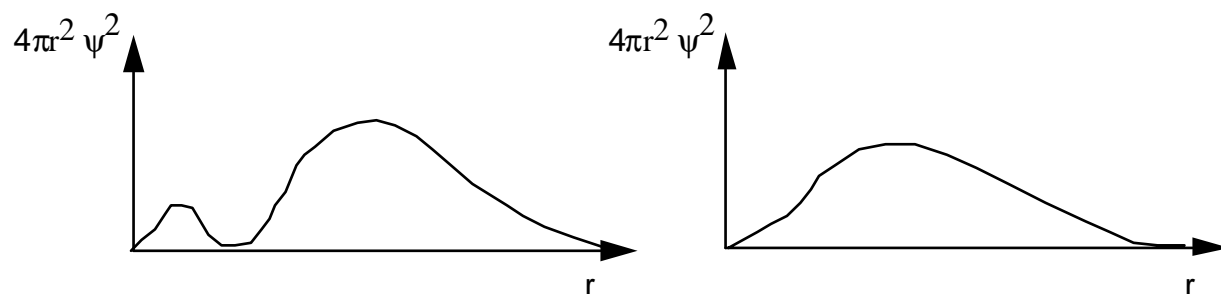
Answer 6 of the following 8 questions. If you answer more than 6, cross out the ones you wish not to be graded. 7 points each.

1. As the internuclear separation, R goes from 0 to ∞ , the overlap integral between two atomic orbitals in a bond goes from _____ to _____.

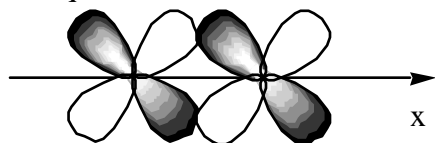
2. Give the expectation value for the total spin angular momentum squared, that is $\langle S^2 \rangle$, for a triplet state.

3. Give the spin multiplicity of the vanadium ground state: $\boxed{\uparrow\downarrow}$ $\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{}\boxed{}$
4s 3d

4. For the two $n=3$ orbitals whose radial distribution functions are shown below, which would feel a larger Z_{eff} ?



5. What is the symmetry of the orbital formed from the side-on overlap of two d orbitals as shown below. This question is answered in three segments. The x-axis is the internuclear axis:



- Is it sigma, pi, or delta?
- Is it bonding or antibonding?
- Is it g or u ?

6. Give the ground state configuration for Mo^{2+} .

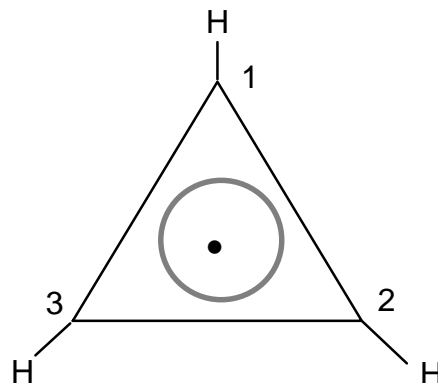
7. An excited state configuration of He is $1s^1 2p^1$. If the spatial wavefunction is $(1s(1)2p(2)-1s(2)2p(1))$, what is/are the allowable spin wavefunction(s)?

8. Would the bond force constant for NO^+ be greater or less than that for NO ? Use MO Theory to explain why?

Part II

9. 12pts) The energy levels and wavefunctions for the cyclopropenyl radical are given below. Calculate the pi bond order for one of the bonds. (Hint: this radical has three pi electrons.)

E	Orbital
$\alpha+2\beta$	$\Psi_1 = 0.577 p_1 + 0.577 p_2 + 0.577 p_3$
$\alpha-\beta$	$\Psi_2 = -0.816 p_1 + 0.408 p_2 + 0.408 p_3$
$\alpha-\beta$	$\Psi_3 = 0.707 p_2 + 0.707 p_3$



10. (12 points) When should you use the 6-311G** basis set instead of a 6-31G* basis set? What does the ** mean?

NH₃ with fixed 90° bond angles HEAT OF FORMATION = 9.09266 KCAL

CARTESIAN COORDINATES		NO	ATOM	X	Y	Z
		1	H	0.0000	0.0000	0.0000
		2	N	1.0296	0.0000	0.0000
		3	H	1.0296	1.0296	0.0000
		4	H	1.0296	0.0000	-1.0296

EIGENVECTORS		ROOT NO.	1	2	3	4	5	6	7
ENERGY			-33.12	-15.03	-15.03	-12.01	4.59	4.78	4.78
S H	1		-0.323	0.478	0.276	-0.231	-0.418	-0.300	0.520
S N	2		-0.807	0.000	0.000	0.459	0.370	0.000	0.000
PX N	2		0.105	-0.520	-0.300	0.457	-0.335	-0.276	0.478
PY N	2		-0.105	0.000	-0.601	-0.457	0.335	-0.552	-0.000
PZ N	2		0.105	0.520	-0.300	0.457	-0.335	-0.276	-0.478
S H	3		-0.323	0.000	-0.552	-0.231	-0.418	0.601	0.000
S H	4		-0.323	-0.478	0.276	-0.231	-0.418	-0.300	-0.520

BONDING CONTRIBUTION OF EACH M.O.

1.3341 1.9743 1.9743 0.6845 -1.9696 -1.9987 -1.9987

BOND-ORDER MATRIX		S-SIGMA	S-SIGMA	P-SIGMA	S-SIGMA	S-SIGMA
		H 1	N 2	N 2	H 3	H 4
S-SIGMA	H 1	0.994				
S-SIGMA	N 2	0.096	0.288			
P-SIGMA	N 2	0.893	0.000	2.679		
S-SIGMA	H 3	0.000	0.096	0.893	0.994	
S-SIGMA	H 4	0.000	0.096	0.893	0.000	0.994

NH₃ with 109° bond angles HEAT OF FORMATION = -7.28191 KCAL

CARTESIAN COORDINATES		NO.	ATOM	X	Y	Z
		1	H	0.0000	0.0000	0.0000
		2	N	0.9989	0.0000	0.0000
		3	H	1.3259	0.9425	0.0000
		4	H	1.3211	-0.4565	-0.8272

EIGENVECTORS		ROOT NO.	1	2	3	4	5	6	7
ENERGY			-32.68	-15.90	-15.88	-10.42	4.22	6.15	6.166
S H	1		-0.313	0.310	0.462	0.158	-0.458	0.510	-0.307
S N	2		-0.829	-0.000	0.000	-0.320	0.457	0.000	-0.000
PX N	2		0.043	-0.38	-0.569	-0.308	-0.138	0.548	-0.331
PY N	2		-0.061	-0.592	0.246	0.434	0.192	-0.201	-0.563
PZ N	2		0.104	-0.189	0.386	-0.732	-0.325	-0.351	-0.194
S H	3		-0.314	-0.555	0.037	0.159	-0.457	0.009	0.596
S H	4		-0.314	0.245	-0.500	0.158	-0.456	-0.522	-0.289

BONDING CONTRIBUTION OF EACH M.O.

1.4127 2.0494 2.0485 0.3620 -2.0257 -1.9238 -1.9232

BOND ORDER MATRIX		S-SIGMA	S-SIGMA	P-SIGMA	S-SIGMA	S-SIGMA
		H 1	N 2	N 2	H 3	H 4
S-SIGMA	H 1	0.982				
S-SIGMA	N 2	0.175	0.526			
P-SIGMA	N 2	0.794	0.000	2.384		
S-SIGMA	H 3	0.003	0.175	0.794	0.982	
S-SIGMA	H 4	0.003	0.175	0.795	0.003	0.982