11. The following are the MO's for fulvene. Using the same MO's calculate the C1-C2   bond order for the first *electronically excited state* of fulvene.

(8 marks)

energy	C1	C2	C3	C4	C5	C6
1.861	-0.439	0.153	0.153	-0.439	0.664	-0.356
-0.618	0.601	0.372	-0.372	-0.601	0	0
-2.115	0.429	0.385	0.385	0.429	0.523	0.247
0.254	-0.350	0.279	0.279	-0.350	-0.190	0.749
-1.000	0	0.5	0.5	0	-0.5	-0.5
1.618	-0.372	0.601	-0.601	0.372	0	0

12. Has the electronic excitation in the previous question strengthened or weakened the C1-C2 bond in fulvene? Explain your reasoning briefly.

(5 marks)

13. Set up the Hückel determinant for the 2-allylmethyl radical.

(5 marks)

14. In an atomic (or molecular system) there are two electrons, 1 and 2, in two orbitals,   and   . Write out expressions for the Coulomb and Exchange integrals, and give a physical explanation for each of them.
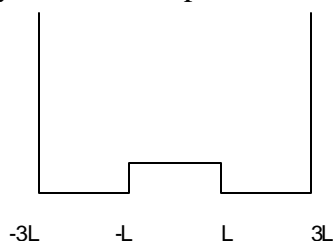
(5 marks)

15. Explain clearly what the terms *conrotatory* and *disrotatory* mean in the context of the Woodward-Hoffman rules of electrocylic reactions.

(5 marks)

16. State the quantum-mechanical virial theorem, which relates the kinetic and potential energies in an atomic or molecular system.

(3 marks)

17. A box has a small symmetric "bump" in the middle (height   ), as shown.

-3L   -L   L   3L

Calculate the first-order perturbed energy of the ground state. Also calculate the mixing coefficient (i.e., the contribution) of the first excited unperturbed state to the first-order perturbed wavefunction.

(12 marks)

18. Sketch a Walsh diagram for the bending of the water molecule. If an electron is promoted from the $1b_1$ orbital (the out-of-plane lone pair) to the next highest orbital, $4a_1$ (note the numbering starts with O 1s being $1a_1$), will the molecule be more or less bent? Justify your answer using the Walsh diagram.

(14 marks)   (100 MARKS TOTAL)

THE END

MCMASTER UNIVERSITY
DURATION: 2 HOURS   APRIL 1999

INSTRUCTOR: DR. A.D. BAIN

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THIS EXAMINATION PAPER INCLUDES 2 PAGES AND 18 QUESTIONS. YOU ARE
RESPONSIBLE FOR ENSURING THAT YOUR COPY OF THE PAPER IS COMPLETE.
BRING ANY DISCREPANCY TO THE ATTENTION OF YOUR INVIGILATOR.

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SPECIAL INSTRUCTIONS: Any electronic calculator may be used, but no other aids are permitted.
USEFUL NUMBERS:
Planck constant (h) = 6.626 x 10^{-34} J sec   Bohr radius (a_0) = 5.292 x 10^{-11} m
1 eV = 8065.5 cm^{-1} = 96.48 $kJ\ mol^{-1}$ = 1.602 x 10^{-19} J $molecule^{-1}$

_____

__1. State Schrödinger's *time-dependent* equation.
(3 marks)

2.   Give the commutation relation among the three angular momentum operators, L_x, L_y and L_z.
(4 marks)

3.   To what point group does *cis*-butadiene belong?
(3 marks)

4.   Sketch the LUMO of *cis*-butadiene.
(4 marks)

5.   State the most general formulation of the Pauli exclusion principle.
(3 marks)

6.   How many radial nodes does the 3p orbital of the hydrogen atom have?
(3 marks)

7.   For a particle-in-a-box, length L, the (unnormalized) wavefunction with the lowest energy is *sin
        ($\pi x/L$)*. However, the function *sin ($\pi x/2L$)* has an expectation value of the Hamiltonian which is
        lower than the eigenvalue of *sin ($\pi x/L$)*. Is this a violation of the Variation Principle? Justify your
        answer.
(5 marks)

8.   Do the operators $x^2\ d^2/dx^2$ and $x\ d/dx$ commute? Show your calculations.
(6 marks)

9.   For the lithium atom, the separation of the $^2S_{1/2}$ state and the $^2P_{1/2}$ state is 14,904 cm^{-1}, whereas
        the same two states are separated by only 2.4 cm^{-1} in the Li^{2+} ion. Explain.
(6 marks)

10.   For the $^2S_{1/2}$ state of the Li atom, give all the spin and orbital angular momentum quantum
        numbers of all three electrons.
(6 marks)