

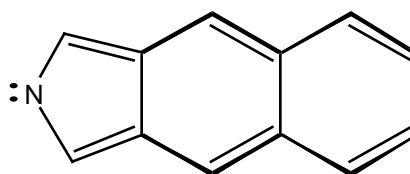
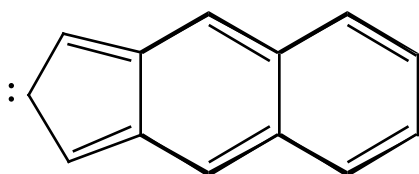
Examination 2 (Communist Style Takehome)

December 4-6, 1995

Chemistry 262

Dr. Jay H. Baltisberger

1. Describe the Hückle approximations used in molecular orbital calculations for the π orbitals and apply these to derive a determinant for the electronic energy in $C_{13}H_9^-$. The molecule $C_{12}H_8N$ would be described by this same matrix to a first order approximation. Describe where improvements could be made in this simple theory by changing terms in the determinant for the $C_{12}H_8N$ molecule. Describe what each integral (α , β) used in these determinants indicates in both words and symbols. (10 points, note that these molecules are fully conjugated, planar and sp^2 hybridized at each atom. Be sure to number the atoms relative to secular determinant columns.)



2. By differentiation of the 2s radial wavefunction, show that it has a minimum in its amplitude and locate it. (5 points)
3. State the orbital degeneracy of the levels in the hydrogen atom that have the energy $-R_H$, $-R_H/9$ and $-R_H/36$. (5 points)
4. Give the possible term symbols for ground state Be, Ti, Sn, and I. (10 points)
5. What atomic terms are possible for the electron configuration $3p^1 3d^1$ and which set is likely to be lowest in energy? (5 points)
6. Describe in a short answer what is required of a molecule to show vibrational transitions. Which of the following molecules may show a vibrational spectrum: (A) H_2 (B) HCl (C) CH_4 (D) CH_2Cl_2 (E) H_2O (F) NH_3 ? (10 points)
7. Determine if the p_x and p_y orbitals are eigenfunctions of l_z . If not, does a linear combination exist that is an eigenfunction of l_z ? (10 points)
8. Construct the five sp^3d orbitals from one 4s, three 4p and one 4d orbitals. (10 points)
9. Which of the following triatomic molecules and ions are expected to be linear: (a) CO_2 , (b) NO_2 , (c) NO_2^+ , (d) SO_2 and (e) H_2O ? Give reasons in each case. (5 points)
10. In the 'free electron molecular orbital' (FEMO) theory, the electrons in a conjugated molecule are treated as independent particles in a box of length L (as in our dye lab). Sketch the form of the two occupied orbitals in butadiene $CH_2=CHCH=CH_2$ predicted by this model and predict the minimum excitation energy of the molecule. The tetraene $CH_2=CHCH=CHCH=CHCH=CH_2$ can be treated as a box of length $8R$, where $R = 140$ pm (as in this case, an extra half bond length is often added at the end of the box to account for delocalization beyond the outer carbon atoms). Calculate the minimum excitation energy of the molecule and sketch the HOMO and LUMO. (10 points)