Introduction to Quantum Chemistry WS 2001/02 Exercises No. 2

Return before Mo evening, Nov. 12, wooden mail-box, AR-K6 left side wall.

Questions hour on

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6) Discuss the rocking vibrations of the central atom A (mass M) of the square planar complex AX_4 (m = mass of X) with single force constants k. Give the formula for ω. Sketch the degenerate level pattern.

7) The distance between two adjacent vibrational levels (the vibrational excitation energy) is (nearly) independent of n, $\Delta E^{vib}_{n \to n+1} = \hbar\omega$. Give the rotational excitation energies $\Delta E^{rot}_{m \to m+1}$.

8) Estimate the π-electron density along the benzene ring for 3 lowest doubly occupied „planar rotator orbitals". a) Using complex canonical orbitals: $\varphi_m = \exp(im\varphi)/\sqrt{2\pi}$, $m = 0, -1, +1$. b) Using real canonical orbitals: $1/\sqrt{2\pi}, \Phi_m = (\varphi_m \pm \varphi_{-m})/\sqrt{2} \sim \cos m\varphi/\sqrt{\pi}$, $\sin m\varphi/\sqrt{\pi}, m = 1$. c) Nonmandatory: Using a localized occupied orbital set $(1 + 2\sin(\varphi + \alpha))/\sqrt{3\pi}$, $\alpha = 0, -120°, 120°$.

9) Estimate the atomic radius. In the energetically lowest, stationary state, the electron would classically vibrate through the nucleus from x = +R to -R. The velocities vary between $+v$ and $-v$, corresponding to momenta $\pm m \cdot v = \pm P$. According to Heisenberg $R \cdot P$ is about $n = 1, 2, \ldots \hbar$. Determine the minimal energy $E = P^2/2m - Z/R$ ($dE/dP = 0$) under this side condition ($P \cdot R = n$). a) Give P, R, T, V, E. b) What is the ratio of $T : V : E$? c) Estimate the effective electronic mass for the 1s state of Hg (m = 1, n = 1, Z = 80). d) Give the relativistic change of orbital radius in %; contraction or expansion?

10) Draw a sketch of the 5d, 5f, 6s, 6p, 6d, 7s, 7p AOs of the Pu atom a) on the energy scale, and b) on the radius scale. Which are „frozen core orbitals", which are „valence-dependent core orbitals", which are the „chemical valence orbitals", which are the „overlapping" orbitals? Which one-electron transitions are „allowed" between the above mentioned n=6 and n=7 one-electron levels?