TC Clausur 17-02-03 Solutions

Feb. 2003

Lsg. 1a) $p \to p/\sqrt{\langle p|p|\rangle} = f \cdot \cos\phi/|f| \cdot \sqrt{\pi} = (e^{i\alpha} \text{ or } \pm 1) \cdot \cos\phi/\sqrt{\pi}$.
From $\langle p_x|p_x\rangle = \int_0^{2\pi} d\phi \cdot f^* \cos\phi \cdot f \cos\phi = |f|^2 \cdot 1/2 \cdot 2\pi$.
$\langle p_x|p_y\rangle = \int_0^{2\pi} d\phi \cdot p_x^* \cdot p_y = \int_0^{2\pi} d\phi \cdot u(\pi) \cdot g(\pi) = 0$; p_x and p_y orthogonal

Lsg. 1b) $\mathbf{P} = -i\hbar \cdot d/dx$; hermitean and linear

Lsg. 1c) $\mathbf{A}$ is hermitean, if for any f, g from the range of given functions, always: $\int_a^b dx \cdot f^*(x) \cdot \mathbf{A}g(x) = \int_a^b dx \cdot (\mathbf{A}f(x))^* \cdot g(x)$, i.e. $\langle f|\mathbf{A}|g\rangle = \langle \mathbf{A}f|g\rangle$

Lsg. 2a) **I** has 4, **II** has 4; HOMO is number 4, is u; LUMO is g; N in the middle stabilizes g; HOMO $\to$ LUMO reduced in **II**; **II** absorbs at smaller ν and longer λ.

Lsg. 2b) $\lambda \sim L$ or $\nu \sim 1/L$. N atoms correspond to N π-electrons. HOMO is no. $N/2$; LUMO is no. $N/2+1$; box energies are $\sim n^2/L^2$; $\Delta E \sim \nu \sim 1/\lambda \sim \{(1+N/2)^2 - (N/2)^2\}/L^2 \sim (1+N)/L^2 \sim L/L^2 \sim 1/L$

Lsg. 2c) $\lambda = 1/\nu = 1/20 \cdot 10^3 \cdot cm = 5.0 \cdot 10^{-7} m = 50_0\, nm$, with 2 significant digits (!). E = 20000 / 8065 eV = 2.4_8 or 2.5 eV = 2.48 * 96.5 kJ/mol = 23_9 or $2.4 \cdot 10^2$ kJ/mol

Lsg. 3a) $l = 1; |L| = \sqrt{l(l+1)}\hbar = \sqrt{2}\hbar = 1.414\hbar$

Lsg. 3b) χ is permutational symmetric. According to Pauli principle ψ must be antisymmetric. E.g. $\phi_a(r_1) \cdot \phi_b(r_2) - \phi_b(r_1) \cdot \phi_a(r_2)$, which has vanishing pair density for $r_1 = r_2$

Lsg. 3c) χ represents 2 “parallel” spins, one up, one down, both pointing to the same side.

Lsg. 3d) If 2 AOs of similar energy overlap, they form 2 MOs, one flat between the nuclei, one steep. — Kinetic energy is expectation value of $\langle \psi \cdot -0.5\psi''\rangle = +0.5\langle \psi'\psi'\rangle$: flat MO has <u>low</u> E_{kin}. — If one atomic electron can move around several nuclei, its Δx is large; for the lowest state, Δp is small; E_{kin} is small. — Electron sharing lowers the energy. — Low orbitals can be filled by up to two electrons. Pair bond results. — At equilibrium, system relaxes, so that virial theorem is fullfilled: $E_{kin} : E_{pot} : E = +1 : -2 : -1$. Electron cloud in bound system is nearer to nuclei (E_{pot} strongly decreased for lowered E), compression increases E_{kin} because of Pauli principle. At the end E_{kin} has <u>risen</u>.

Lsg. Ca) Diameter of atoms is 3 – 4 Å. I.e. 3 Atoms per nm. So: an atomic nano-cluster of a few to several 10 nm has several 10 to a million atoms. Small Au or C nanoparticles have 50 to 100 atoms. Small metal clusters tend to stick together. Cover the surface by ligands (|S-R) or in matrix.

Lsg. Cb) Two sharp metal tips. Connect Molecule, e.g. through S or O atoms. Conjugated π-chains, homo- or hetero-atomic, possibly doped with electron donors or acceptors.

Lsg. Cc) A nanoparticle has a spectrum similar to a large molecule, or a particle in a box. Lines shifted with respect to small molecule or bulk. One particle has sharp lines with broad side wings. Many particles yield a broad overlaid spectrum without details.