

1. Let $\psi_s = f(r)$ (where $r = |\vec{r}|$) represent a normalized spherical atomic s function. **(a)** Show that for a set of p functions, the choices $\{\psi_x = \sqrt{3}f(r)x/r$ and similar for $y, z\}$, are all normalized, mutually orthogonal, and orthogonal to ψ_s . **(b)** Show that of all possible functions that “point” in the x-direction (in the sense that ψ is normalized and $|\psi(\vec{r} = r\hat{x})|^2$ is maximized), the best choice is $\psi = (1/2)\psi_s + (\sqrt{3}/2)\psi_x$. **(c)** Show that the function $|1\rangle = (\psi_s + \psi_x + \psi_y + \psi_z)/2$ points optimally in the (111) direction. **(d)** Show that the function $|2\rangle = (\psi_s - \psi_x - \psi_y + \psi_z)/2$ is orthogonal to $|1\rangle$ and points optimally in the $(\bar{1}\bar{1}1)$ direction. Construct two more functions $|3\rangle$ and $|4\rangle$ that form a set of 4 mutually orthogonal and optimally pointing functions. **(e)** Sketch the four functions and show that they point to the corners of a tetrahedron. These functions are a basis for “sp³ bonding.”

2. From the set of functions $\{\psi_s, \psi_x, \psi_y\}$, construct a new set of 3 orthogonal functions that are equivalent under rotations of 120°. Some hints: You are constructing a unitary transformation, but that information is not particularly helpful. What is helpful is that the “s” part of the states $\{|1\rangle, |2\rangle, |3\rangle\}$ must be the same in all three states (why?). And, you must be able to “invert” the process and reconstruct $\{\psi_s, \psi_x, \psi_y\}$ from $\{|1\rangle, |2\rangle, |3\rangle\}$. Finally, it is not necessary, but it is certainly sensible to choose $|1\rangle$ to point (perhaps not optimally) along \hat{x} . These functions are a basis for “sp² bonding. The (so far) unused function ψ_z is available for “ π -bonding.” What does this have to do with formaldehyde (O=CH₂)?

3. **LCAO bands in 1d.** Atoms of type “a” are at positions $x_{na} = na$, and have a non-degenerate s level of energy $E_0 - \Delta$ and wave function $|na\rangle = \psi_a(x - x_{na})$. Atoms of type “b” are at positions $x_{nb} = na + \frac{1}{2}a$, with a non-degenerate p_x level of energy $E_0 + \Delta$ and wave function $|nb\rangle = \psi_b(x - x_{nb})$.

The illustration to the right, from Ibach and Lüth, has the correct geometry if you change labels from y to x . The system is periodic with period a . The levels are all

orthogonal to each other. The Hamiltonian matrix elements are $\langle na|H|n'a\rangle = (E_0 - \Delta)\delta_{nn'}$, $\langle nb|H|n'b\rangle = (E_0 + \Delta)\delta_{nn'}$, and $\langle na|H|n'b\rangle = V$ if $|n'b\rangle$ is just to the right of $|na\rangle$ ($n = n'$). **(a)** By symmetry, what is the matrix element $\langle na|H|n'b\rangle$ if $|n'b\rangle$ is just to the left of $|na\rangle$ ($n' = n - 1$)? **(b)** Explain why it is sensible to have V positive, given the attractive potential that electrons experience from atoms. **(c)** Derive the band structure. **(d)** For $E_0 = 0$ and $\Delta = 1$ eV and $V = 1$ eV, plot energy versus wave-vector in the Brillouin zone, with the energy and k -axis dimensions given. **(e)** Sketch the density of states versus energy.

