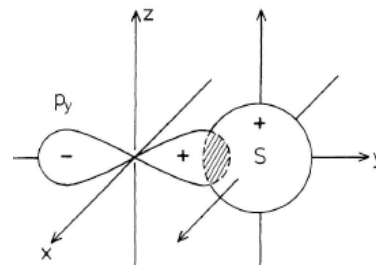


1. Let  $\psi_s = f(r)$  (where  $r = |\vec{r}|$ ) represent a normalized spherical atomic s function. **(a)** Show that for a set of p functions, the choices  $\{\psi_x = \sqrt{3}f(r)x/r$  and similar for  $y, z\}$ , are all normalized, mutually orthogonal, and orthogonal to  $\psi_s$ . **(b)** Show that of all possible functions that “point” in the x-direction (in the sense that  $\psi$  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 “sp<sup>3</sup> 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 “sp<sup>2</sup>” bonding. The (so far) unused function  $\psi_z$  is available for “π-bonding.” What does this have to do with formaldehyde (O=CH<sub>2</sub>)?

1. **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.

4. Here is **problem 1.11** from Ibach and Lüth (see below).

**1.11** As a simple quantum mechanical model for the van der Waals interaction consider two identical harmonic oscillators (oscillating dipoles) at a separation  $R$ . Each dipole consists of a pair of opposite charges whose separations are  $x_1$  and  $x_2$ , respectively, for the two dipoles. A restoring force  $f$  acts between each pair of charges.

- Write down the Hamiltonian  $\mathcal{H}_0$  for the two oscillators without taking into account electrostatic interaction between the charges.
- Determine the interaction energy  $\mathcal{H}_1$  of the four charges.
- Assuming  $|x_1| \leq R$ ,  $|x_2| \leq R$  approximate  $\mathcal{H}_1$  as follows

$$\mathcal{H}_1 \approx -\frac{2e^2 x_1 x_2}{R^3} \quad \checkmark$$

- Show that transformation to normal coordinates

$$x_s = \frac{1}{\sqrt{2}} (x_1 + x_2),$$

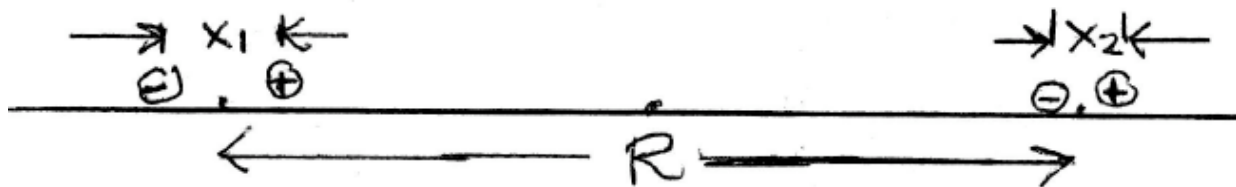
$$x_a = \frac{1}{\sqrt{2}} (x_1 - x_2)$$

decouples the total energy  $\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1$  into a symmetric and an anti-symmetric contribution.

- Calculate the frequencies  $\omega_s$  and  $\omega_a$  of the symmetric and antisymmetric normal vibration modes. Evaluate the frequencies  $\omega_s$  and  $\omega_a$  as Taylor series in  $2e^2/(fR^3)$  and truncate the expansions after second order terms.
- The energy of the complete system of two interacting oscillators can be expressed as  $U = -\frac{1}{2}\hbar (\omega_s + \omega_a)$ . Derive an expression for the energy of the isolated oscillators and show that this is decreased by an amount  $c/R^6$  when mutual interaction (bonding) occurs.

This problem does a good job getting at the mechanism of van der Waals bonding. I do not find the wording very clear, and will try to illuminate. Also, on p.16, Ibach and Lüth state that the source of van der Waals interaction is "charge fluctuations in atoms due to zero point motion." This is correct once you understand that they are not talking about zero point motion of nuclear coordinates, but of electron behavior. This is not standard terminology, in my experience. A better way to say it, and this problem illustrates it well, is that the *source of van der Waals interactions is higher-order modifications of quantum electron charge fluctuations that occur in response to quantum charge fluctuations of other atoms*. It is definitely a quantum effect, not found in classical physics.

The geometry of this problem is 1-dimensional. Here is a coordinate system.



The oscillator displacements  $x_1$ ,  $x_2$  are positive when the + charge is to the right of the - charge, and vary symmetrically around 0. The interaction energy  $H_1$  should not include interactions between the + and - charges (+ and - |e|) of a single oscillator, just between charges on different oscillators.