

Materials 286G: Bonding in homonuclear diatomics and the extension to semiconductors:

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This discussion follows P. W. Atkins, Physical Chemistry, and P. A. Cox.

The frontier orbitals on the semiconductor AB have the wavefunctions ϕ_A and ϕ_B which are assumed to be normalized. Then by linear combination of atomic orbitals, the resulting wavefunction is given by:

$$\psi = c_A\phi_A + c_B\phi_B \quad (1)$$

The energies associated with ψ are given by

$$E = \frac{\langle \psi^* | H | \psi \rangle}{\langle \psi^* | \psi \rangle} = \frac{\langle c_A\phi_A | H | c_A\phi_A \rangle + \langle c_B\phi_B | H | c_B\phi_B \rangle + 2\langle c_A\phi_A | H | c_B\phi_B \rangle}{\langle c_A\phi_A | c_A\phi_A \rangle + \langle c_B\phi_B | c_B\phi_B \rangle + 2\langle c_A\phi_A | c_B\phi_B \rangle} \quad (2)$$

We have used $\psi^* = \psi$ since we assume that the starting wavefunctions and the coefficients are real. We define $E_A = \langle \phi_A | H | \phi_A \rangle$, $E_B = \langle \phi_B | H | \phi_B \rangle$, a covalent energy term, $V_{AB} = \langle \phi_A | H | \phi_B \rangle$, and the overlap integral $S_{AB} = \langle \phi_A | \phi_B \rangle$. Due to normalization, $\langle \phi_A | \phi_A \rangle = 1$ etc. This leads us to

$$E = \frac{c_A^2 E_A + c_B^2 E_B + 2c_A c_B V_{AB}}{c_A^2 + c_B^2 + 2c_A c_B S_{AB}} \quad (3)$$

The variational theorem suggests that the best guess of the energy is the minimum value. This allows us to set:

$$\frac{\partial E}{\partial c_A} = 0 \quad \& \quad \frac{\partial E}{\partial c_B} = 0 \quad (4)$$

Going through the calculus, one obtains the simultaneous equations:

$$\begin{aligned} (E_A - E)c_A + (V_{AB} - ES_{AB})c_B &= 0 \\ (V_{AB} - ES_{AB})c_A + (E_B - E)c_B &= 0 \end{aligned} \quad (5)$$

The conditions for the equation to be soluble are given by the *secular determinant*:

$$\begin{vmatrix} (E_A - E) & (V_{AB} - ES_{AB}) \\ (V_{AB} - ES_{AB}) & (E_B - E) \end{vmatrix} = 0 \quad (6)$$

One simplification is to set the overlap integral to zero: $S_{AB} = 0$. The determinant then expands to a quadratic, and solves to

$$E = (E_A + E_B)/2 \pm [V_{AB}^2 + (E_A - E_B)^2/4]^{1/2} \quad (7)$$

The smaller energy corresponds to the HOMO, the middle of the valence band, and the larger energy to the LUMO, the middle of the conduction band. The difference in energies between these is given by:

$$\Delta E = [V_{AB}^2 + (E_A - E_B)^2]^{1/2} \quad (8)$$

Defining $E_i = E_A - E_B$ and $E_c = 2V_{AB}$, this simplifies to:

$$\Delta E = (E_i^2 + E_c^2)^{1/2} \quad (9)$$

In the Phillips–van Vechten picture, E_c is determined for the elemental semiconductors, C, Si, Ge, Sn, as 14.0 eV, 6.0 eV, 5.6 eV and 4.3 eV. The values of E_i (in eV) are obtained from the differences in the Phillips–van Vechten electronegativities of the different elements. These are close to Pauling’s values, especially for the non–metals.

Addendum

If we assume that the two atoms A and B are the same, and $E_A = E_B$, and we don’t ignore overlap, we obtain for the bonding and antibonding energy levels:

$$E_{\pm} = \frac{E_A \pm V_{AB}}{1 \pm S_{AB}} \quad (10)$$

The negative sign corresponds to the antibonding energy level and the positive sign to bonding. Note that antibonding is larger in magnitude when the overlap is non-zero.