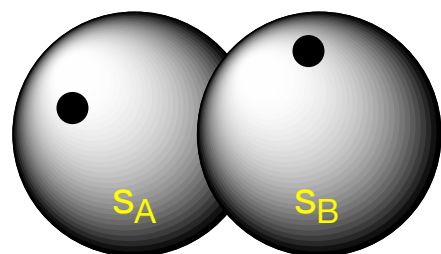# Meaning of Structures
The valence bond approach

- Localised, atomic orbitals
- Two singlet spin-coupled orbitals represent bond

$$\Phi = N\left[\left|s_A(1)\overline{s_B(2)}\right| - \left|\overline{s_A(1)}s_B(2)\right|\right]$$

- Build structure wavefunctions Φ
- Form molecular wavefunction as a superposition of structures:

$$\Psi = \sum_i c_i \Phi_i$$

- Optimise orbitals used to build Φ_i and structure coefficients c_i
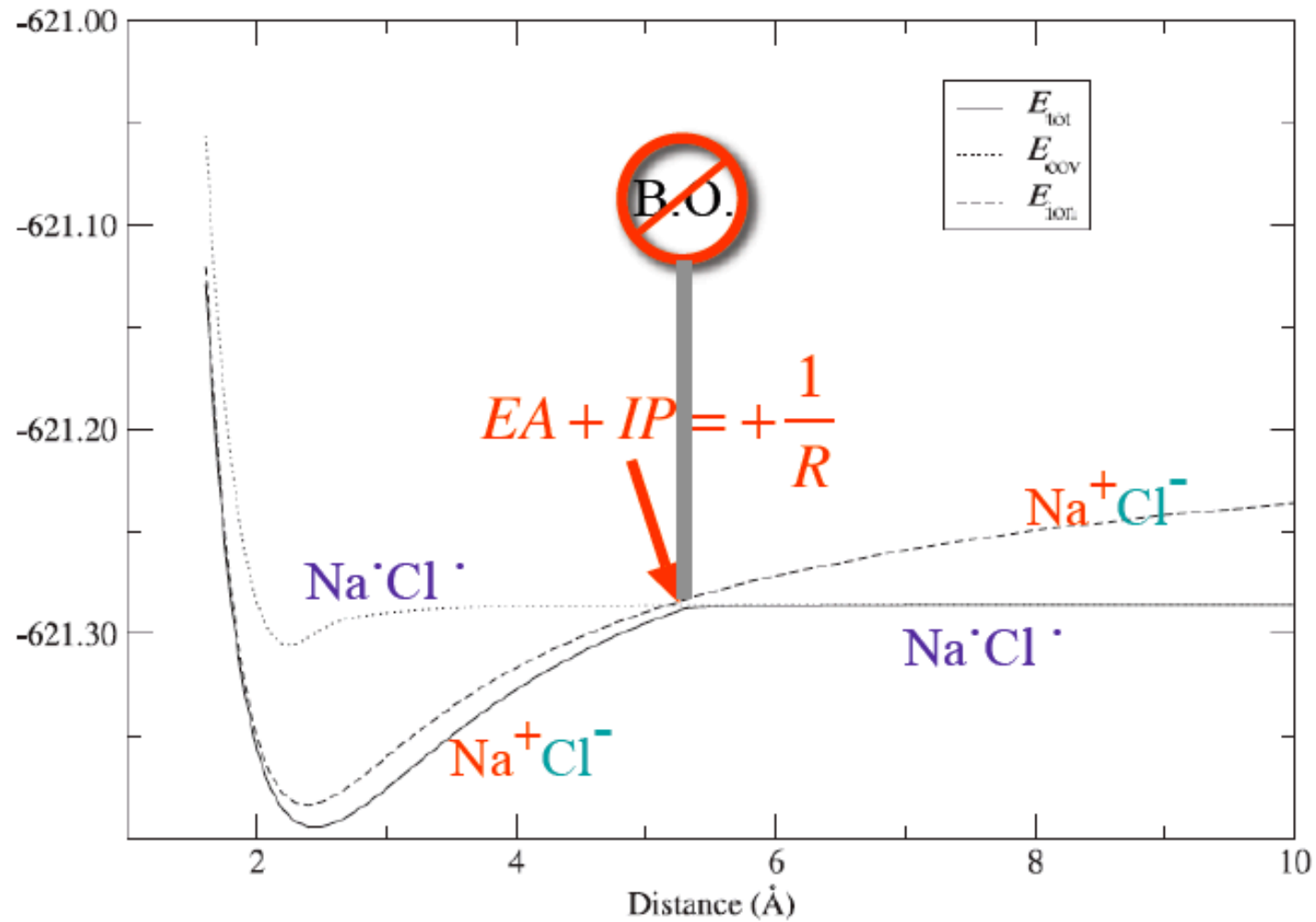
Polar and apolar bonds

- Covalent contributions
  - Electrons equally shared between nuclei
    - Orbitals may be strictly atomic or delocalised

$$X \!\!-\!\! Y$$

- Ionic contributions
  - Electron transfer from one nucleus to the other
    - Orbitals are necessary localised on fragment

$$\Psi = c_1 \Phi_{X-Y} + c_2 \Phi_{X^- Y^+} + c_3 \Phi_{X^+ Y^-}$$

Born-Oppenheimer3 NaCl

Si-Cl bond dissociation

$(H_3C)_3Si$ —— Cl

varies from 1.4 Å to 10.0 Å

Gasphase geometries (GVB-1PP/6-31G*)

not important

$\Psi = $ $(H_3C)_3Si$—Cl $+$ $Cl^{\ominus}$ $^{\oplus}Si(CH_3)_3$ $+$ $Cl^{\oplus}$ $^{\ominus}Si(CH_3)_3$

Covalent

Ionic

Total

$sp^2 - sp^3$

1 s orbital + 2 p orbitals =

3 sp^2 orbitals

1 s orbital + 3 p orbitals =

4 sp^3 orbitals
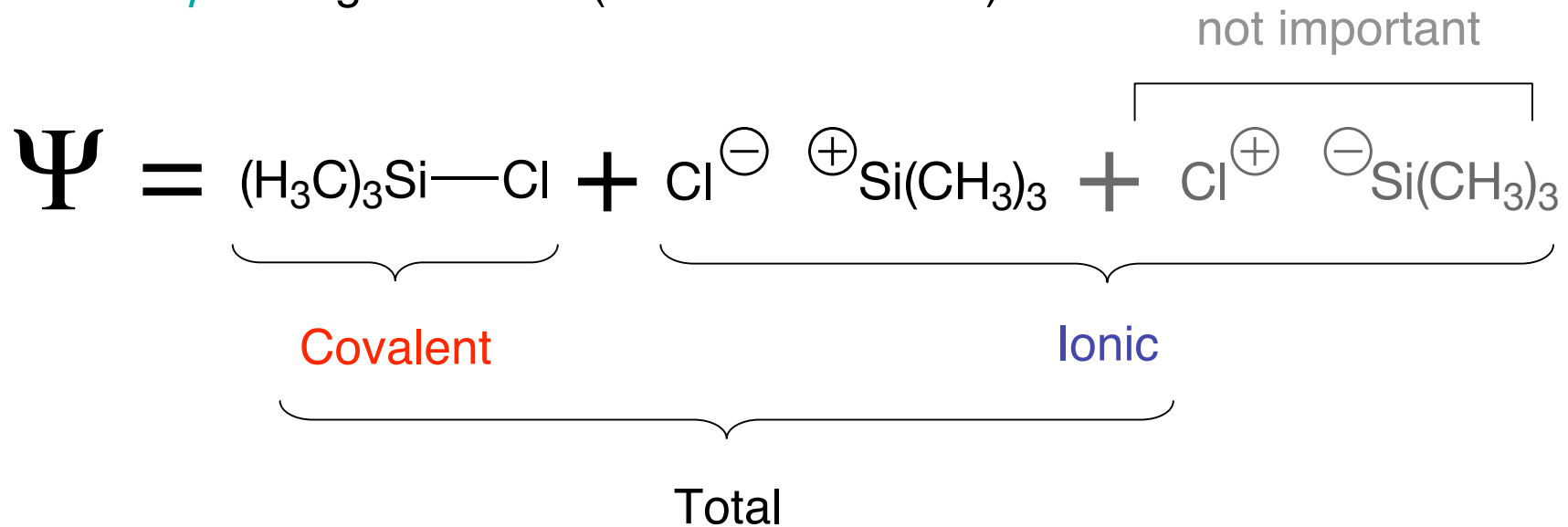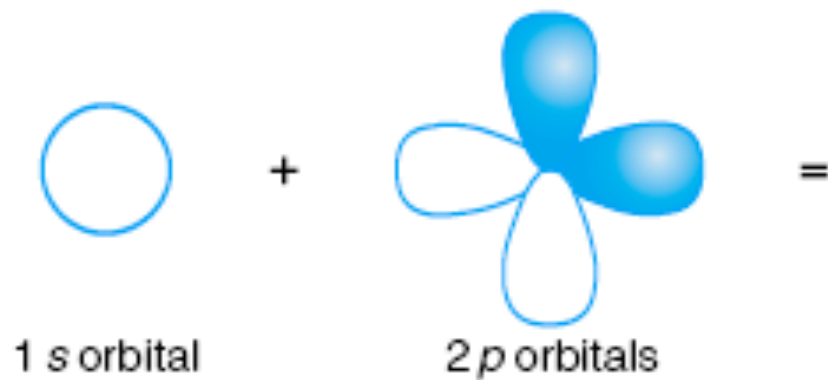
6 electrons

"flat"
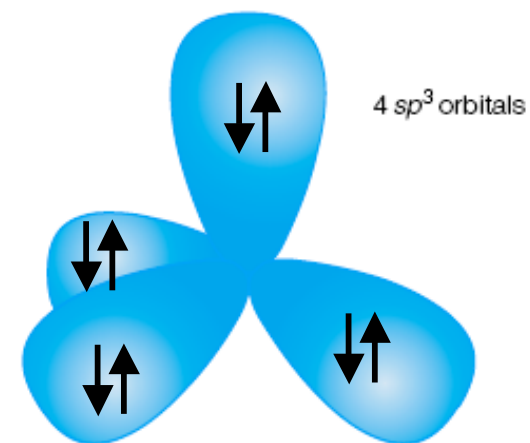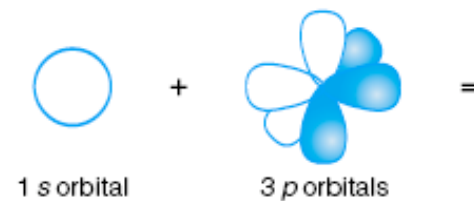
8 electrons

"tetrahedral"

Dissociation curves

large change in geometry
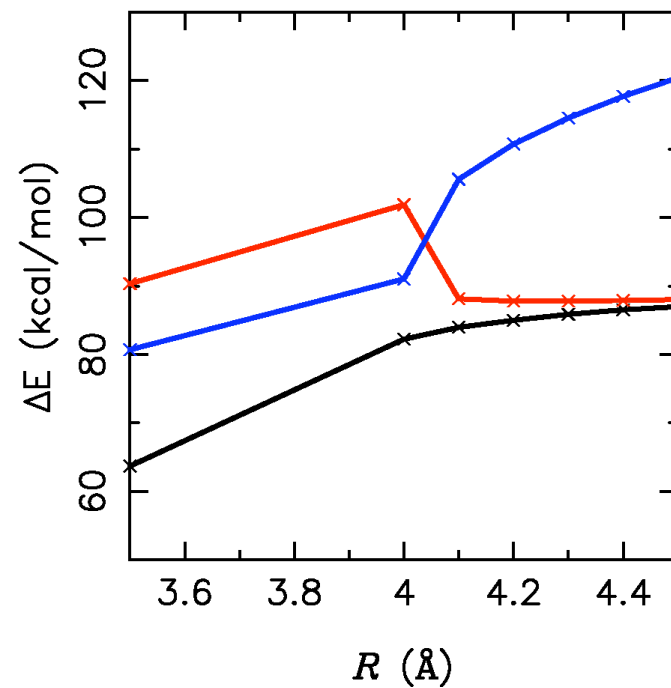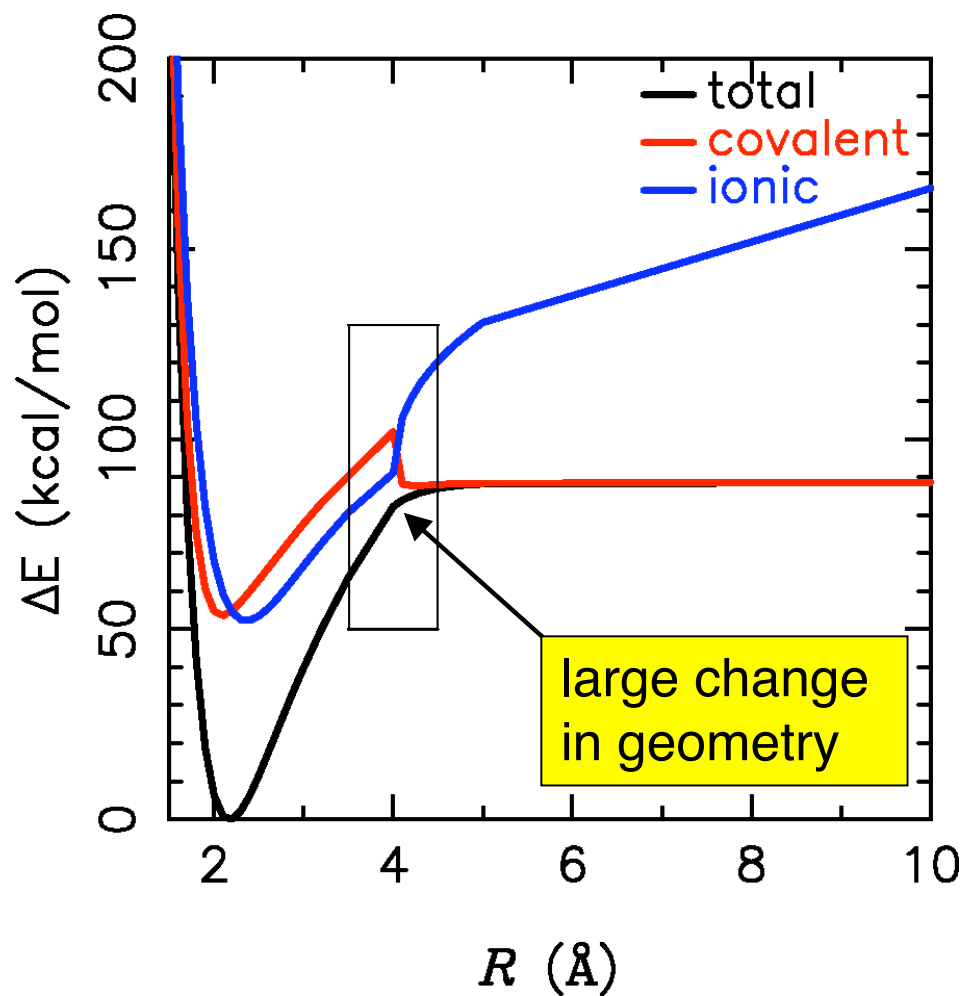
Discontinuities in individual-structure-curves
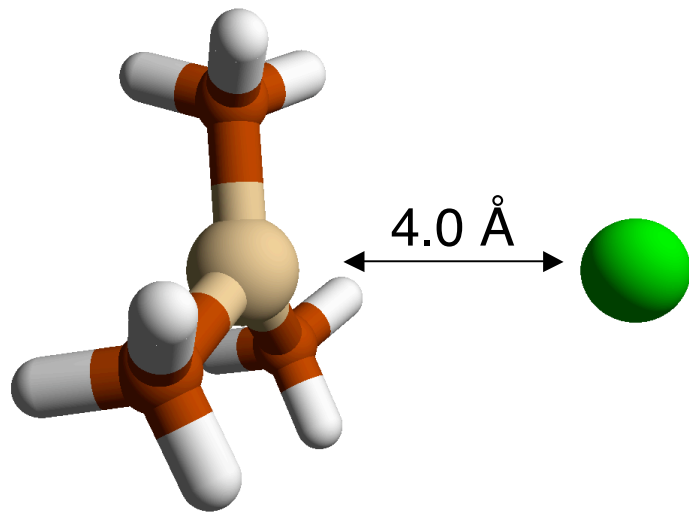
- (H$_3$C)$_3$-Si nearly co-planar
  - ∠C-Si-C-C: 166°
- 'Cationic' geometry
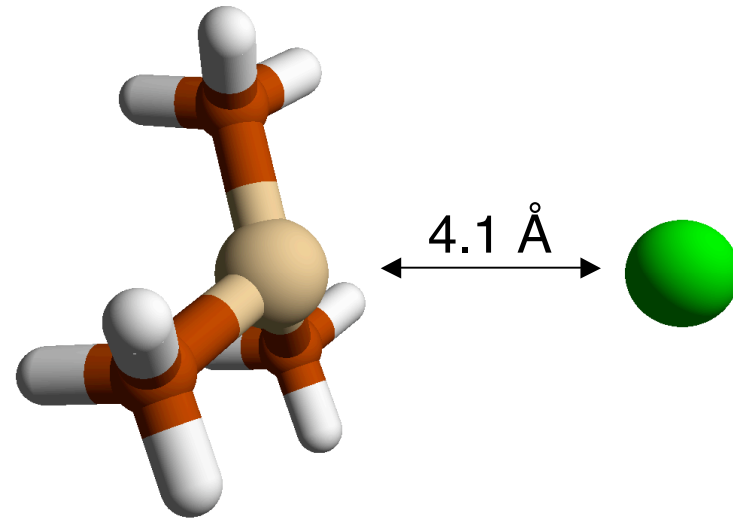
- (H$_3$C)$_3$-Si tetrahedral
  - ∠C-Si-C-C: 133°
- 'Radical' geometry

Individual ionic or covalent dissociations are not represented
by the VB ionic/covalent curves

Nature of valence bond structures are determined by the whole molecular environment