

Lecture 16: Unitary Equivalence and Localized Orbitals

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Unitary Transformations of Orbitals

- Consider Slater determinant Φ with N orthonormal occupied orbitals $\{\phi_i\}$
- Unitary transformation of occupied orbitals into themselves:

$$\tilde{\phi}_i(x) = \sum_j U_{ij} \phi_j(x),$$

$$\mathbf{U}^\dagger \mathbf{U} = 1$$

- The $\{\tilde{\phi}_i\}$ also form a basis of N orthonormal occupied orbitals
- Chemical significance?

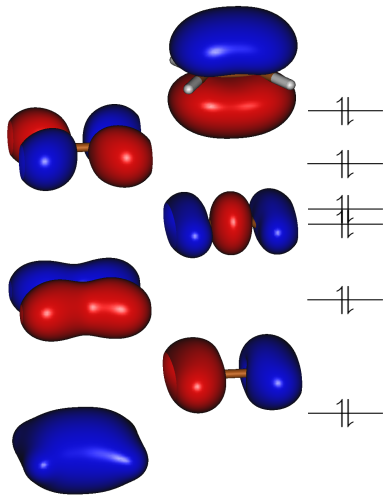
Transformation of Φ

- Slater determinant with transformed orbitals $\{\tilde{\phi}_i\}$:

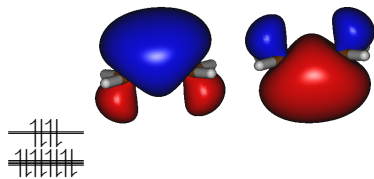
$$\begin{aligned}\tilde{\Phi}(x_1, \dots, x_N) &= \frac{1}{\sqrt{N!}} \begin{vmatrix} \tilde{\phi}_1(x_1) & \tilde{\phi}_1(x_2) & \dots & \tilde{\phi}_1(x_N) \\ \tilde{\phi}_2(x_1) & \tilde{\phi}_2(x_2) & \dots & \tilde{\phi}_2(x_N) \\ \dots & \dots & \vdots & \dots \\ \tilde{\phi}_N(x_1) & \tilde{\phi}_N(x_2) & \dots & \tilde{\phi}_N(x_N) \end{vmatrix} \\ &= \frac{1}{\sqrt{N!}} \mathbf{U} \begin{vmatrix} \phi_1(x_1) & \phi_1(x_2) & \dots & \phi_1(x_N) \\ \phi_2(x_1) & \phi_2(x_2) & \dots & \phi_2(x_N) \\ \dots & \dots & \vdots & \dots \\ \phi_N(x_1) & \phi_N(x_2) & \dots & \phi_N(x_N) \end{vmatrix} \\ &= |\mathbf{U}| \Phi(x_1, \dots, x_N) = e^{i\phi} \Phi(x_1, \dots, x_N)\end{aligned}$$

- Φ and $\tilde{\Phi}$ are identical up to a complex phase factor $e^{i\phi}$, $\phi \in \mathbb{R}$
- N -electron observables are invariant under unitary transformations of occupied orbitals

Example: Ethylene Valence Orbitals



Canonical (delocalized)



(4x)

Boys Localized

Canonical vs. Localized Orbitals

- Canonical Orbitals

- ▶ Related to vertical ionization/electron attachment: Orbital energies approximate IP, obtained from diagonalizing (effective) one-electron Hamiltonian
- ▶ Useful for photoelectron spectroscopy, redox chemistry, perturbation theory
- ▶ Delocalized

- Localized orbitals

- ▶ Maximize orbital dipole moment (Boys), Coulomb energy (Edmiston-Rüdenberg), etc.
- ▶ Orbital energies ill-defined, no simple chemical meaning!
- ▶ “Banana bonds”; may be used to define atomic “hybridization state”
- ▶ Fairly local but beware of “orthogonality tails”
- ▶ Not unique, sometimes not well defined
- ▶ May be used to partition properties into fragment contributions

- Canonical vs. localized orbitals merely reflect different choices of

Hund's Localization Condition

- Under what conditions can all occupied orbitals be localized into 2e2c bonds (“perfect localization”)?
- The ground state of molecules with perfectly localized electronic structure is well described by a single valence-bond structure
- Hund's condition for perfect localization: For every atom, the following must hold:

$$N_{AO} = N_B = N_V$$

N_{AO} : Number of valence AOs available for bonding (excluding lone pairs)

N_B : Number of (2e2c) bonds

N_V : Number of valence electrons contributing to bonds

- Classification of chemical bonds:
 1. $N_V < N_{AO}$: Hypovalent compounds, electron deficiency, 2e-multi-center bonds, e.g. H_3^+ , boranes, metal clusters, metals
 2. $N_V = N_{AO}$: Normalvalent compounds, localized 2e2c bonds
 3. $N_V > N_{AO}$: Hypervalent compounds, electron excess, hypervalence and/or 4e-multi-center bonds, e.g. hydrogen bonds, FHF^- , XeF_2

Examples

- C_2H_4 : Normalvalent, perfectly localizable
- H_2 : Normalvalent, perfectly localizable, since $N_{AO} = N_B = N_V = 2$ for O after excluding lone pairs
- B_2H_6 : Not localizable, because $N_{AO} = 4$, $N_V = 3$, $N_B = 3$ or 4. B_2H_6 is hypovalent with bridging 2e3c bonds
- SO_3 : Not localizable, since $N_{AO} = 4$ (no valence d orbitals!), $N_V = N_B = 6$ for S