

Figure 6.3 The MO formed by interaction between the antisymmetric combination of H 1s orbitals and the oxygen p_x orbital (see also Figure 6.7). Bonding interactions are enhanced by mixing a small amount of O d_{xz} character into the MO

A Rationale for Adding Polarization (i.e. higher angular momentum) Basis Functions

From Christopher J. Cramer, *Essentials of Computational Chemistry*, 2nd Edition; Wiley: Chichester, England, 2004.

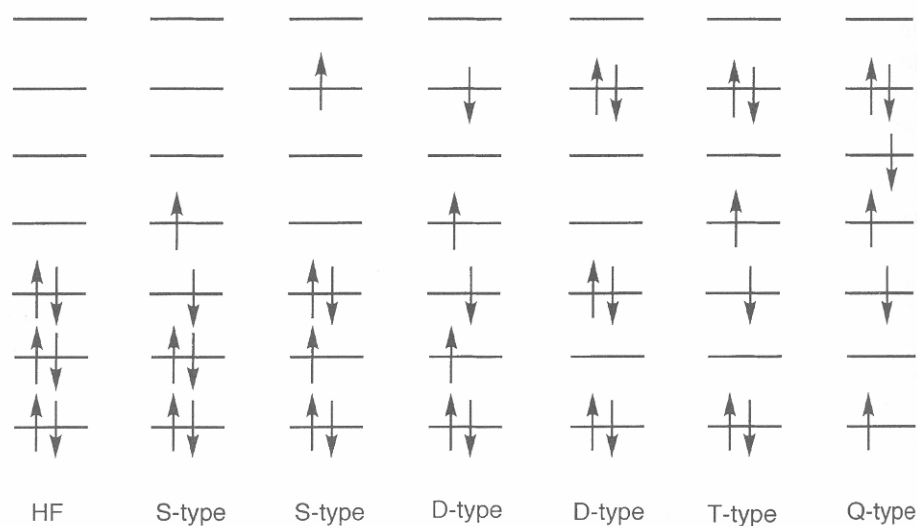


Figure 4.1 Excited Slater determinants generated from a HF reference

Beyond Hartree-Fock (HF) Theory:
Treating Electron Configuration by
Adding Antibonding Character to a
Ground-State Wavefunction

From Frank Jensen, *Introduction to Computational Chemistry*, Wiley: Chichester, England, 1999.

Quantum Chemical Methods

“Model Chemistry”—any combination of level of theory + basis set

Level of Electron Correlation →

	HF	MP2	MP4(SDQ)	CCSD(T)	...	Full CI
6-31G [†]				X		
6-31+G(d,p)			X			
6-311+G(2df,2p)				X		
⋮						
Complete Basis Set		X				Complete CI

↘

Saving Grace: One can compute geometry and frequencies with a “cheaper” model chemistry with little loss in accuracy

Diligence: One High-Level Single-Point Energy

Artifice: A Set of Single-Point Energies (e.g. CBS-QB3, Gx, MC-Gx)

Indulgence: Density Functional Theory (DFT) (e.g. B3LYP, MPW1K)