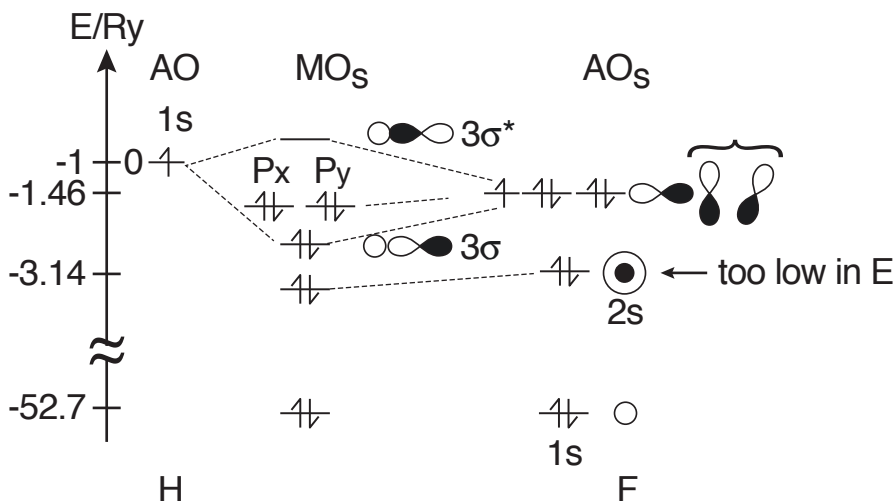


Potential surfaces of molecules:

Example: HF with MO basis



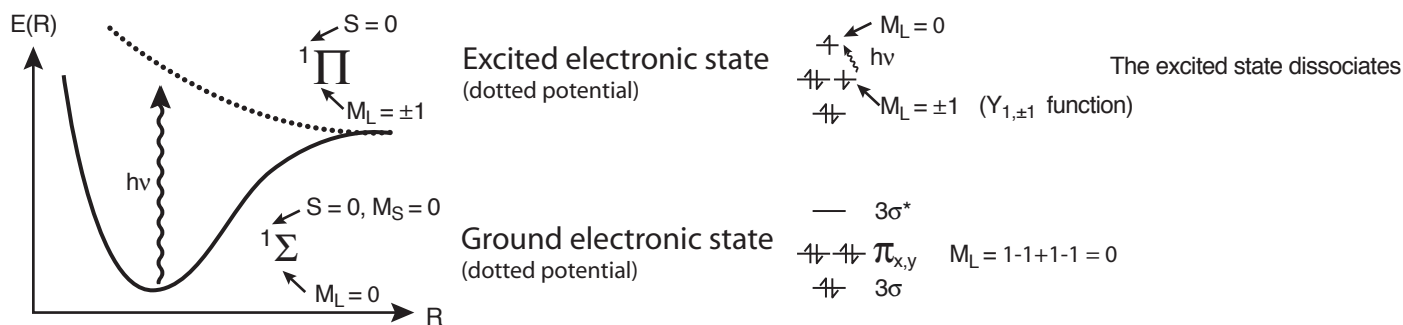
Diagonalizing 1-electron Hamiltonian in atomic orbital basis ϕ_m yields reasonable MO basis functions ϕ_i $|3\sigma\rangle$ and $|3\sigma^*\rangle$

$$\langle 1s_H | \hat{H}_{1e^-} | 2p_{x,y} \rangle = 0 \text{ but}$$

$$\langle 1s_H | \hat{H}_{1e^-} | 2p_z \rangle = H_{S1P2}$$

$$\underline{H}_{1e^-} \approx \begin{pmatrix} H_{1s} & H_{1s,2p_z} & \text{small} \dots \\ H_{1s,2p_z} & H_{2p_z} & 0 \dots \\ \text{small} & 0 & \dots \end{pmatrix}$$

diagonalizing the 2 x 2 matrix yields approx. $|3\sigma\rangle$ MO basis functions



Actual Hartree-Fock SCF potential surfaces calculated by Bender and Davidson in 1968:

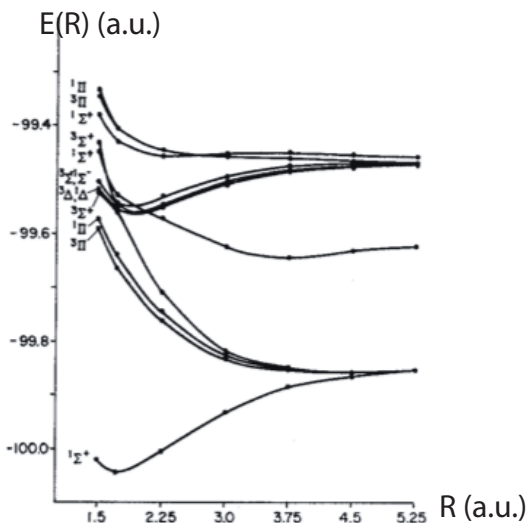


FIG. 2. Potential energy (hartrees) for several states of the hydrogen fluoride molecule as a function of internuclear distance (bohrs).

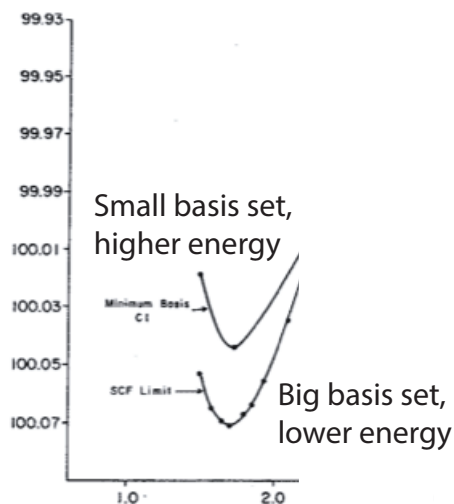


FIG. 3. Comparison of Cade's SCF calculation with the present results for the ground state of HF.