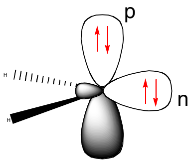
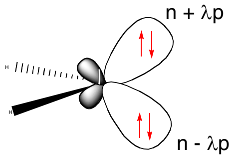
The lone pairs of H_2O



Ψ_{MO}



Ψ_{VB}

1) $\Psi_{MO} = |n\bar{n}p\bar{p}|$, $\Psi_{VB} = |(n-\lambda p)(\bar{n}-\lambda\bar{p})(n+\lambda p)(\bar{n}+\lambda\bar{p})|$.

2) $\Psi_{VB} = |(n\bar{n} - \lambda p\bar{n} - \lambda n\bar{p} + \lambda p\bar{p})(n\bar{n} + \lambda p\bar{n} + \lambda n\bar{p} + \lambda p\bar{p})|$

$$= |n\bar{n}n\bar{n}| + \lambda|n\bar{n}p\bar{n}| + \lambda|n\bar{n}n\bar{p}| + \lambda^2|n\bar{n}p\bar{p}|$$
$$-\lambda|p\bar{n}n\bar{n}| - \lambda^2|p\bar{n}p\bar{n}| - \lambda^2|p\bar{n}n\bar{p}| - \lambda^3|p\bar{n}p\bar{p}|$$
$$-\lambda|n\bar{p}n\bar{n}| - \lambda^2|n\bar{p}p\bar{n}| - \lambda^2|n\bar{p}n\bar{p}| - \lambda^3|n\bar{p}p\bar{p}|$$
$$+\lambda^2|p\bar{p}n\bar{n}| + \lambda^3|p\bar{p}p\bar{n}| + \lambda^3|p\bar{p}n\bar{p}| + \lambda^4|p\bar{p}p\bar{p}|$$

After eliminating all determinants having two orbitals with the same spin, there remains : $\Psi_{VB} = \lambda^2|n\bar{n}p\bar{p}| - \lambda^2|p\bar{n}n\bar{p}| - \lambda^2|n\bar{p}p\bar{n}| + \lambda^2|p\bar{p}n\bar{n}|$.

After permuting the columns and changing signs accordingly, there remains :

$\Psi_{VB} = 4\lambda^2|n\bar{n}p\bar{p}| = \Psi_{MO}$ (if one includes normalization factors).

3) $\Phi_1 = |(n-\lambda p)(\bar{n}-\lambda\bar{p})(n+\lambda p)|$, $\Phi_2 = |(n-\lambda p)(\bar{n}+\lambda\bar{p})(n+\lambda p)|$ (putting the orbitals in maximum correspondance).

4) Φ_1 and Φ_2 differ by only one orbital, (n-λp) in Φ_1 which becomes (n+λp) in Φ_2 . Therefore the matrix element $\langle\Phi_1|H|\Phi_2\rangle$ is a simple β integral, necessarily negative.
=> The lowest ionized state is $\frac{1}{\sqrt{2}}(\Phi_1+\Phi_2)$ while the higher ionized state is $\frac{1}{\sqrt{2}}(\Phi_1-\Phi_2)$.

5) $\Phi_1 = |n\bar{n}n| - \lambda|p\bar{n}n| - \lambda|n\bar{p}n| + \lambda^2|p\bar{p}n| + \lambda|n\bar{n}p| - \lambda^2|p\bar{n}p| - \lambda^2|n\bar{p}p| + \lambda^3|p\bar{p}p|$

$\Phi_1 = +2\lambda^2|p\bar{p}n| + 2\lambda|n\bar{n}p|$

In the same way, one shows that $\Phi_2 = -2\lambda^2|p\bar{p}n| + 2\lambda|n\bar{n}p|$. It follows that :

$(\Phi_1+\Phi_2) \propto |n\bar{n}p|$ (lowest ionized state in MO theory)

$(\Phi_1-\Phi_2) \propto |p\bar{p}n|$ (higher ionized state in MO theory) .

It is concluded that 1) VB theory yields two ionization potentials for H_2O, in agreement with experiment, and 2) that these ionization potentials are exactly the same as the ones found in elementary MO theory.