Two-Orbital Tight-Binding for H_2^+: Variational Derivation

Setup

Let ϕ_a and ϕ_b be real, normalized basis functions on nuclei a and b:

$$\langle\phi_a|\phi_a\rangle = \langle\phi_b|\phi_b\rangle = 1, \qquad S \equiv S_{ab} = \langle\phi_a|\phi_b\rangle = S_{ba}.$$

Define matrix elements $H_{ij} = \langle\phi_i|\hat{H}|\phi_j\rangle$ and $S_{ij} = \langle\phi_i|\phi_j\rangle$ for $i, j \in \{a, b\}$. Seek $\psi = c_a\phi_a + c_b\phi_b$ with coefficient vector $\mathbf{c} = (c_a, c_b)^\mathsf{T}$.

Variational principle ⇒ generalized eigenproblem

The variational energy functional (AKA Rayleigh quotient) is

$$E(\mathbf{c}) = \frac{\langle\psi|\hat{H}|\psi\rangle}{\langle\psi|\psi\rangle} = \frac{\sum_{ij} c_i H_{ij} c_j}{\sum_{ij} c_i S_{ij} c_j}.$$

Introduce a Lagrange multiplier E to enforce $\langle\psi|\psi\rangle = 1$ and stationarize

$$\mathcal{L}(\mathbf{c}; E) = \sum_{ij} c_i H_{ij} c_j - E \sum_{ij} c_i S_{ij} c_j.$$

Setting $\partial\mathcal{L}/\partial c_k = 0$ for $k = a, b$ gives

$$\sum_j (H_{kj} - ES_{kj})\, c_j = 0 \quad \Rightarrow \quad (H - ES)\,\mathbf{c} = \mathbf{0},$$

with

$$H = \begin{pmatrix} H_{aa} & H_{ab} \\ H_{ab} & H_{bb} \end{pmatrix}, \qquad S = \begin{pmatrix} 1 & S \\ S & 1 \end{pmatrix}.$$

Component equations and secular determinant

Written by rows,

$$\begin{aligned} (H_{aa} - E)\, c_a + (H_{ab} - ES)\, c_b &= 0, \\ (H_{ab} - ES)\, c_a + (H_{bb} - E)\, c_b &= 0. \end{aligned} \tag{1}$$

Nontrivial solutions require the secular determinant to vanish:

$$\det(H - ES) = \begin{vmatrix} H_{aa} - E & H_{ab} - ES \\ H_{ab} - ES & H_{bb} - E \end{vmatrix} = 0.$$

Expanding,

$$(1 - S^2)E^2 - \big[(H_{aa} + H_{bb}) - 2SH_{ab}\big]\, E + (H_{aa}H_{bb} - H_{ab}^2) = 0. \tag{2}$$

The two roots are the MO energies in the $\{\phi_a, \phi_b\}$ subspace.

Homonuclear (H_2^+) limit

For identical centers: $H_{aa} = H_{bb} \equiv \alpha$, $H_{ab} \equiv \beta$, overlap S. Then the determinant condition reduces to

$$(\alpha - E)^2 - (\beta - ES)^2 = 0 \implies \alpha - E = \pm(\beta - ES),$$

and the energies are

$$E_\pm = \frac{\alpha \pm \beta}{1 \pm S}.$$

From either equation in (1),

$$\frac{c_b}{c_a} = -\frac{\alpha - E}{\beta - ES} = \begin{cases} 1, & E = E_+ \quad \text{(bonding)}, \\ -1, & E = E_- \quad \text{(antibonding)}. \end{cases}$$

Thus (unnormalized) eigenvectors are $(1,1)^\mathsf{T}$ and $(1,-1)^\mathsf{T}$, and the normalized MOs are

$$\psi_+(\mathbf{r}) = \frac{\phi_a(\mathbf{r}) + \phi_b(\mathbf{r})}{\sqrt{2(1+S)}}, \qquad \psi_-(\mathbf{r}) = \frac{\phi_a(\mathbf{r}) - \phi_b(\mathbf{r})}{\sqrt{2(1-S)}}.$$

Checks

Orthogonal-basis limit $S \to 0$: $E_\pm \to \alpha \pm \beta$, $\psi_\pm \to (\phi_a \pm \phi_b)/\sqrt{2}$. Dissociation (large R): $S \to 0$, $\beta \to 0$, so $E_\pm \to \alpha$.