OVERVIEW of SOME ASPECTS OF HMO Theory

Hamiltonian operator — eigenvalue

$$\mathcal{H}\Psi = E\Psi$$

eigenfunction

SCHRÖDINGER EQ.

$\times$ by Ψ^* & $\int d\tau$ →

bra-ket notation

$$E = \frac{\langle\Psi|\mathcal{H}|\Psi\rangle}{\langle\Psi|\Psi\rangle}$$

LCAO-MO

$$\Psi_i = \sum_r c_r \chi_r$$

ith MO; AO at atom r; coeff. at atom r

$$E_i = \frac{\sum_r \sum_s c_r c_s \langle\chi_r|\mathcal{H}|\chi_s\rangle}{\sum_r \sum_s c_r c_s \langle\Psi_r|\Psi_s\rangle}$$

Want smallest E subject to the condition that the VARIATION THEOR. HOLDS TRUE →

$$E_{true} \leq E_{calc}$$

VARIATION THEOREM

MINIMIZE E

$$\left(\frac{\partial E}{\partial c}\right) = 0;\quad \frac{\partial^2 E}{\partial c^2} > 0$$

$$\sum_s (H_{rs} - E_i S_{rs})\, c_s = 0$$

for $r = 1, 2, 3, \ldots$

SECULAR EQUATIONS

Ex.

$$0 = (H_{11} - ES_{11})c_1 + (H_{12} - ES_{12})c_2 + (H_{13} - ES_{13})c_3$$
$$0 = (H_{21} - ES_{21})c_1 + (H_{22} - ES_{22})c_2 + (H_{23} - ES_{23})c_3$$
$$0 = (H_{31} - ES_{31})c_1 + (H_{32} - ES_{32})c_2 + (H_{33} - ES_{33})c_3$$

Let $H_{rr} = \alpha_r = \alpha = \int \chi_r \mathcal{H} \chi_r\, d\tau = \langle\chi_r|\mathcal{H}|\chi_r\rangle \equiv$ COULOMB INTEGRAL

$H_{rs} = \beta_{rs} = \beta = \int \chi_r \mathcal{H} \chi_s\, d\tau = \langle\chi_r|\mathcal{H}|\chi_s\rangle \equiv$ RESONANCE INTEGRAL

$S_{rs} = \delta_{rs} = \begin{cases} 0, & r \neq s \\ 1, & r = s \end{cases} = \langle\chi_r|\chi_r\rangle$ } ZDO

$$0 = \sum_s (H_{rs} - E_i S_{rs})c_s = (H_{rr} - E_i S_{rr})c_r + \sum_{\substack{s \\ r\neq s}} (H_{rs} - E_i S_{rs})c_s$$

$$0 = (\alpha - E_i)c_r + \sum_{\substack{s \\ r\neq s}} \beta c_s$$

ANOTHER FORM FOR SECULAR EQUATIONS. THIS ONE INVOLVES α's, β

$\div$ by β & let $\frac{\alpha - E_i}{\beta} = x_i$

$$0 = x_i c_r + \sum_{\substack{s \\ (r\neq s)}} c_s$$

→ SOLVE FOR x_i. Then, use x_i to determine c_r's