

# Variational method

$$\hat{H}|\psi_0\rangle = E_0|\psi_0\rangle \quad \text{(ground state)}$$

$$\langle\psi|\hat{H}|\psi\rangle = E_0\langle\psi|\psi\rangle$$

$$E_0 = \frac{\langle\psi|\hat{H}|\psi\rangle}{\langle\psi|\psi\rangle} \quad E = \frac{\langle\psi|\hat{H}|\psi\rangle}{\langle\psi|\psi\rangle} \quad \text{expectation value (Rayleigh quotient)}$$

$$E = \frac{\langle\psi|\hat{H}|\psi\rangle}{\langle\psi|\psi\rangle} \geq E_0$$

$$\hat{H}|\psi_i\rangle = E_i|\psi_i\rangle \quad |\psi\rangle = \sum c_i|\psi_i\rangle \quad \langle\psi_i|\psi_j\rangle = \delta_{ij}$$

$$\langle\psi|\psi\rangle = \langle\sum c_i\psi_i|\sum c_j\psi_j\rangle = \dots = \sum |c_i|^2$$

$$\langle\psi|\hat{H}|\psi\rangle = \langle\sum c_i\psi_i|\hat{H}|\sum c_j\psi_j\rangle = \dots = \sum |c_i|^2 E_i$$

$$E = \frac{\langle\psi|\hat{H}|\psi\rangle}{\langle\psi|\psi\rangle} = \frac{\sum |c_i|^2 E_i}{\sum |c_i|^2} \geq \frac{\sum |c_i|^2 E_0}{\sum |c_i|^2} = E_0$$

$$\delta E = \delta \left( \frac{\langle\psi|\hat{H}|\psi\rangle}{\langle\psi|\psi\rangle} \right) = 0$$

$$\delta E = \frac{\delta\langle\psi|\hat{H}|\psi\rangle \cdot \langle\psi|\psi\rangle + \langle\psi|\hat{H}|\psi\rangle \cdot \delta\langle\psi|\psi\rangle}{(\langle\psi|\psi\rangle)^2}$$

$$= \frac{(\delta\psi|\hat{H}|\psi) + \langle\psi|\hat{H}|\delta\psi) \cdot \langle\psi|\psi\rangle + \langle\psi|\hat{H}|\psi\rangle (\delta\psi|\psi) + \langle\psi|\delta\psi\rangle}{(\langle\psi|\psi\rangle)^2}$$

$$= \frac{\langle\delta\psi|\hat{H}|\psi\rangle + \langle\psi|\hat{H}|\delta\psi\rangle + \langle\psi|\hat{H}|\psi\rangle \langle\delta\psi|\psi\rangle + \langle\psi|\delta\psi\rangle \langle\psi|\hat{H}|\psi\rangle}{\langle\psi|\psi\rangle^2} + \text{c.c.} = 0$$

$$\langle\delta\psi|\hat{H}|\psi\rangle - \frac{\langle\psi|\hat{H}|\psi\rangle}{\langle\psi|\psi\rangle} \langle\delta\psi|\psi\rangle = 0$$

$$\langle\delta\psi|\hat{H} - E\hat{1}|\psi\rangle = 0$$

1) whole Hilbert-space  $\hat{H}|\psi\rangle = E|\psi\rangle$

2) restricted Hilbert-space  $\hat{H}|\psi\rangle = E|\psi\rangle$

$$E(\psi_0 + \delta\psi) \approx E(\psi_0) + \delta E + \mathcal{O}(\delta\psi^2)$$

opt.  $\delta(\text{dipol moment}) \sim \delta\psi$

