Sheet 7

$$\frac{\partial E_\lambda}{\partial \lambda} = \left\langle \psi(\lambda) \middle| \frac{\partial H_\lambda}{\partial \lambda} \middle| \psi(\lambda) \right\rangle$$

↳ Ehrenfest ? → doesn't work because it's derivation is from the Schrödinger Eq.

→ Variationsrechnung?

$\frac{\partial}{\partial\lambda} H|n\rangle =$

$H|n\rangle = (H^0 + \lambda H^1)|n\rangle$

$\frac{\partial}{\partial\lambda} H|n\rangle = \frac{\partial}{\partial\lambda} H^0|n\rangle + \frac{\partial}{\partial\lambda}\lambda H^1|n\rangle$

$= H^0 \frac{\partial}{\partial\lambda}|n\rangle + \left(\frac{\partial}{\partial\lambda}H^1\right)|n\rangle + \frac{\partial}{\partial\lambda}|n\rangle$

$= (H^0 + \mathbb{1})|n\rangle + \frac{\partial}{\partial\lambda} H^1|n\rangle \qquad \Big|\ |n\rangle = \sum_{i=0}^{\infty} \lambda^i |n_i\rangle = \lambda \sum_{i=0}^{\infty} (i+1)\lambda|n_{i+1}\rangle$

$= \lambda(H^0 + \mathbb{1})$

$$\frac{\partial}{\partial\lambda}\langle\psi(\lambda)|\hat{H}_\lambda|\psi(\lambda)\rangle = \int d^3r \, \frac{\partial}{\partial\lambda}\psi^*(\lambda) H \psi(\lambda)$$

$$= \int d^3r \left(\frac{\partial}{\partial\lambda}\psi^*(\lambda)\right) H\psi(\lambda) + \psi^* \frac{\partial}{\partial\lambda} H\psi$$

$$= \int d^3r \quad — \quad " \quad — \quad + \psi^*\left(\frac{\partial}{\partial\lambda}H\right)\psi + \psi^* H \frac{\partial}{\partial\lambda}\psi$$

$$= \left\langle \frac{\partial}{\partial\lambda}\psi \middle| H \middle| \psi \right\rangle + \left\langle \psi \middle| \frac{\partial}{\partial\lambda} H \middle| \psi \right\rangle + \overbrace{\left\langle \psi \middle| H \middle| \frac{\partial}{\partial\lambda}\psi \right\rangle}^{= \langle H\psi | \frac{\partial}{\partial\lambda}\psi\rangle}$$

$$= \left\langle \frac{\partial}{\partial\lambda} H \right\rangle + E\left\langle \frac{\partial}{\partial\lambda}\psi \middle| \psi \right\rangle + E\left\langle \psi \middle| \frac{\partial}{\partial\lambda}\psi \right\rangle$$

$$= \left\langle \frac{\partial}{\partial\lambda} H \right\rangle + E \frac{\partial}{\partial\lambda}\overbrace{\langle\psi|\psi\rangle}^{1} = \left\langle \frac{\partial}{\partial\lambda} H \right\rangle$$

$$H_{\text{nucleus},I} = \sum_i \frac{Z_i e^2}{|r_i - R_I|} + \sum_{I\neq J} \frac{Z_I Z_J e^2}{|R_I - R_J|} \rightarrow -\frac{\partial}{\partial R} H_I = F_I = \sum_i \frac{Z_i e^2 \, |r_i - R_I|}{|r_i - R_I|^3} + \sum_{I\neq J} \frac{Z_I e^2 |R_J - R_I|}{|R_I - R_J|^3}$$

$\sum_i \rightarrow \int n(r)\, d^3r$

$$\Rightarrow F_I = \int n(r) \frac{Z_i e^2 \, |r_i - R_I|}{|r_i - R_I|^3} d^3r + \sum_{I\neq J} \frac{Z_I e^2 |R_J - R_I|}{|R_I - R_J|^3}$$