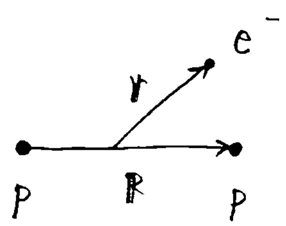
§. Generator Coordinate Method

0. Di-atomic molecule

H_2^+



$$H = \frac{\mathbb{P}^2}{2\mu} + \frac{\mathbb{p}^2}{2m_e} + V\left(\mathbb{r} + \frac{\mathbb{R}}{2}\right) + V\left(\mathbb{r} - \frac{\mathbb{R}}{2}\right) + V_{pp}(R)$$

$$H\,\Psi(\mathbb{R}, \mathbb{r}) = E\,\Psi(\mathbb{R}, \mathbb{r})$$

Born - Oppenheimer Approximation

· first fix R, and solve eq. for $\mathbb{r}$

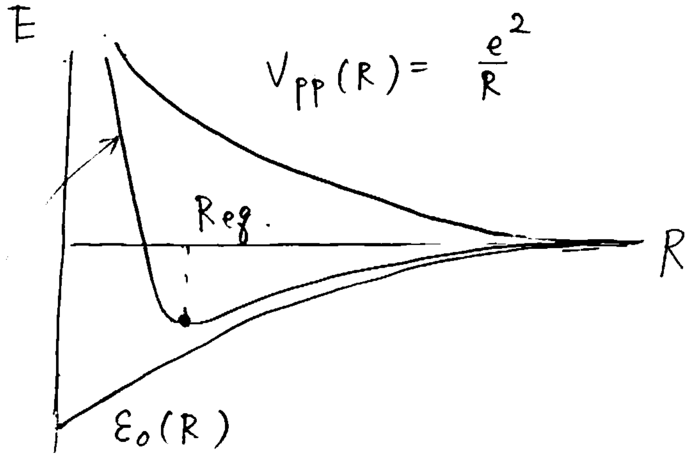
$$\left[\frac{\mathbb{p}^2}{2m_e} + V\left(\mathbb{r} + \frac{\mathbb{R}}{2}\right) + V\left(\mathbb{r} - \frac{\mathbb{R}}{2}\right)\right] \phi_0(\mathbb{r}; \mathbb{R})$$

$$= \varepsilon_0(R)\, \phi_0(\mathbb{r}; \mathbb{R})$$

· Then solve for R

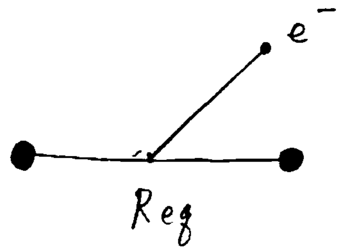
$$\left[\frac{\mathbb{P}^2}{2\mu} + V(R) + \varepsilon_0(R)\right] \psi(\mathbb{R}) = E\,\psi(\mathbb{R})$$

or minimize $\quad V(R) + \varepsilon_0(R)$



$V_{pp}(R) + \varepsilon_0(R)$

- zero-th approximation



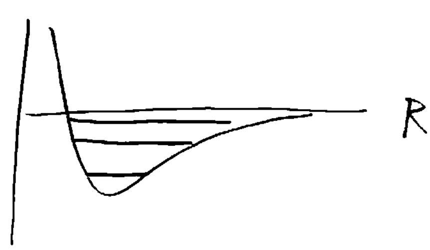
$$\Psi(\mathbb{R}, \mathbb{r}) = \phi_0(\mathbb{r}, \mathbb{R}_{eq}) \times \delta(\mathbb{R} - \mathbb{R}_{eq})$$

- zero point fluctuation

$$\Psi(\mathbb{R}, \mathbb{r}) \approx \int d\mathbb{R}' \, f_0(\mathbb{R}') \underbrace{\delta(\mathbb{R} - \mathbb{R}') \phi_0(\mathbb{r}, \mathbb{R}')}$$

- vibrational motion

$$\Psi_n(\mathbb{R}, \mathbb{r}) = \int d\mathbb{R}' \, f_n(\mathbb{R}') \, \delta(\mathbb{R} - \mathbb{R}') \, \phi_0(\mathbb{r}, \mathbb{R}')$$



1. Constraint Hartree - Fock

$$H = \sum_i \frac{\mathbf{p}_i^2}{2m} + \frac{1}{2} \sum_{i,j} v(\mathbf{r}_i, \mathbf{r}_j)$$

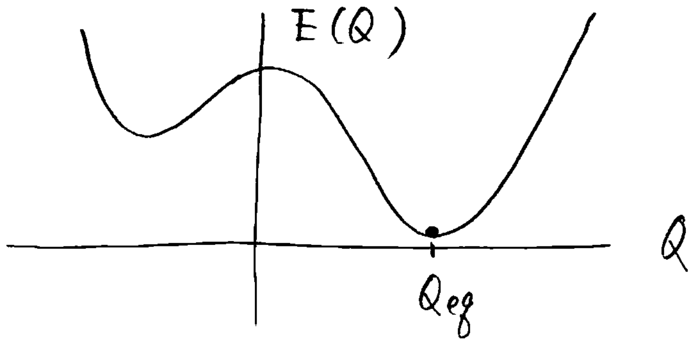
minimize H with a Slater determinant under a condition of $\langle \hat{Q} \rangle = Q$.

$$\rightarrow \frac{\delta}{\delta \varphi_i} \langle \Psi | H - \lambda \hat{Q} | \Psi \rangle = 0.$$

$$\Psi(\mathbf{r}_1, \cdots, \mathbf{r}_A) = \frac{1}{\sqrt{A!}} \begin{vmatrix} \varphi_1(\mathbf{r}_1) & \cdots & \varphi_1(\mathbf{r}_A) \\ \vdots & & \vdots \\ \varphi_A(\mathbf{r}_1) & \cdots & \varphi_A(\mathbf{r}_A) \end{vmatrix}$$

$$\rightarrow \quad \Psi_Q(\mathbf{r}_1, \cdots, \mathbf{r}_A)$$

$$E(Q) = \langle \Psi_Q | H | \Psi_Q \rangle$$



· minimize $E(Q)$ w.r.t. Q $\rightarrow Q_{eq}$

$\quad \Psi_{HF}(\mathbf{r}_1, \cdots, \mathbf{r}_A) = \Psi_{Q_{eq}}(\mathbf{r}_1, \cdots, \mathbf{r}_A)$

2. Generator Coordinate Method (GCM)

assume
$$|\Phi\rangle = \int dQ\, f(Q)\, |\Psi_Q\rangle$$

Q : generator coordinate

$f(Q)$: weight function

(to be determined by the variational principle)

$$\delta \frac{\langle \Phi | H | \Phi \rangle}{\langle \Phi | \Phi \rangle} = 0$$

$$\rightarrow \boxed{\int dQ' \langle \Psi_Q | H | \Psi_{Q'} \rangle f(Q) = E \int dQ' \langle \Psi_Q | \Psi_{Q'} \rangle f(Q')}$$

Hill-Wheeler equation

(note)

$$\langle \Psi_Q | \Psi_{Q'} \rangle \neq \delta(Q - Q')$$

formally,

$$\mathcal{H} f = E n f$$

$$\mathcal{H}(Q,Q') = \langle \Psi_Q | H | \Psi_{Q'} \rangle$$
$$n(Q,Q') = \langle \Psi_Q | \Psi_{Q'} \rangle$$

↓

$$\underbrace{\frac{1}{\sqrt{n}} \mathcal{H} \cdot \frac{1}{\sqrt{n}}}_{\mathcal{H}_{\text{eff}}} \cdot \underset{\substack{\parallel\!\!| \\ g}}{\sqrt{n} f} = E \underset{\substack{\parallel\!\!| \\ g}}{\sqrt{n} f}$$

$g(Q)$: collective wave function

§. Time-dependent Hartree-Fock (TDHF)

- time-dependent variational principle:

$$\delta \int dt \, \langle \Phi | i\hbar \partial_t - H | \Phi \rangle = 0$$

$\downarrow$

$$i\hbar \dot{\varphi}_i(\mathbf{r},t) = h[\rho(t)]\, \varphi_i(\mathbf{r},t)$$

$$= -\frac{\hbar^2}{2m} \nabla^2 \varphi_i(\mathbf{r},t) + \left[\int d\mathbf{r}' \, \rho(\mathbf{r}',t)\, V(\mathbf{r},\mathbf{r}')\right] \varphi_i(\mathbf{r},t) + \text{Fock term}$$

$$\rho(\mathbf{r},t) = \sum_{i:occ} \varphi_i^*(\mathbf{r},t)\, \varphi_i(\mathbf{r},t)$$

- alternative representation

$$i\hbar \dot{\rho} = [h, \rho]$$

$$\rho(\mathbf{r},\mathbf{r}';t) = \sum_{i:occ} \varphi_i(\mathbf{r},t)\, \varphi_i^*(\mathbf{r}',t)$$

∘ semi-classical limit

Wigner - transform

$$f(q,p) = \int d^3s \, e^{-ip\cdot s/\hbar} \, \rho\left(q+\frac{s}{2}, q-\frac{s}{2}\right)$$

(note) $(\hat{A}\cdot\hat{B})_W(\vec{q},\vec{p})$

$$= \int ds \, e^{-ip\cdot s/\hbar} \left\langle q+\frac{s}{2} \middle| \hat{A}\hat{B} \middle| q-\frac{s}{2} \right\rangle$$

$$= \cdots = A_W(q,p) \, e^{\frac{i\hbar}{2}\overleftrightarrow{\Lambda}} \, B_W(q,p)$$

where $\overleftrightarrow{\Lambda} = \overleftarrow{\nabla}_q \overrightarrow{\nabla}_p - \overleftarrow{\nabla}_p \overrightarrow{\nabla}_q$

$\downarrow$

$$\frac{1}{\hbar}[A,B]_W = \frac{1}{\hbar}\left(A_W e^{\frac{i\hbar}{2}\overleftrightarrow{\Lambda}} B_W - \underbrace{B_W e^{\frac{i\hbar}{2}\overleftrightarrow{\Lambda}} A_W}_{= A_W e^{-\frac{i\hbar}{2}\overleftrightarrow{\Lambda}} B_W}\right)$$

$$= \frac{2i}{\hbar} A_W \sin\left(\frac{\hbar}{2}\overleftrightarrow{\Lambda}\right) B_W$$

$$i\hbar \frac{\partial}{\partial t} \hat{\rho} = [h, \hat{\rho}]$$

$$\xrightarrow[\text{W.T.}]{} \cancel{i} \frac{\partial}{\partial t} f(\vec{q}, \vec{p}) = \frac{1}{\hbar}[h, \hat{\rho}]_W$$

$$= \frac{2\cancel{i}}{\hbar} \underbrace{h_W(\vec{q}, \vec{p})}_{\frac{\mathbb{P}^2}{2m} + V(\vec{q})} \sin\left(\frac{\hbar}{2}\overleftrightarrow{\Lambda}\right) f(\vec{q}, \vec{p})$$

(note)

$$\mathbb{P}^2 \sin\left(\frac{\hbar}{2}\overleftrightarrow{\Lambda}\right) f = \mathbb{P}^2 \cdot \frac{\hbar}{2}\left(-\overleftarrow{\nabla}_p \cdot \overrightarrow{\nabla}_q\right) f$$

$$= -\hbar\, \mathbb{P} \cdot \nabla_q f$$

$$\downarrow$$

$$\boxed{\left(\frac{\partial}{\partial t} + \frac{\mathbb{P}}{m} \cdot \nabla_q\right) f(\vec{q}, \vec{p}) = \frac{2}{\hbar} V(\vec{q}) \sin\left(\frac{\hbar}{2}\overleftrightarrow{\Lambda}\right) f(\vec{q}, \vec{p})}$$

to the lowest order of $\hbar$:

$$\text{rhs} = \frac{2}{\hbar} V(\vec{q}) \cdot \frac{\hbar}{2} \overleftrightarrow{\Lambda} f(\vec{q}, \vec{p})$$

$$= (\nabla V) \cdot \nabla_p f(\vec{q}, \vec{p})$$

$$\downarrow$$

$$\left(\frac{\partial}{\partial t} + \frac{\mathbb{P}}{m} \cdot \nabla_q - (\nabla V) \cdot \nabla_p\right) f(\vec{q}, \vec{p}) = 0$$

(Boltzmann equation)