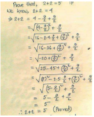

Approximate methods in Quantum Mechanics

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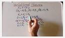
PHYSICAL CHEMISTRY I

Index



Variation theorem

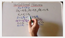
$$\hat{H}\psi_k = E_k\psi_k \qquad k = 1, 2, \ldots \qquad E_1 \leq E_2 \leq \ldots$$

$$\phi = \sum_{k=1} a_k \psi_k$$

$$\langle \phi | \phi \rangle = \langle \sum_{j=1} a_j \psi_j | \sum_{k=1} a_k \psi_k \rangle$$

$$= \sum_{j=1} a_j^* \sum_{k=1} a_k \cancel{\langle \psi_j | \psi_k \rangle} \rightarrow \delta_{j,k}$$

$$= \sum_{j=1} a_j^* a_j = \sum_{j=1} |a_j|^2 = 1$$



Variation theorem

$$
\begin{aligned}
\langle\phi|\hat{H}|\phi\rangle &= \langle\sum_{j=1} a_j\psi_j|\hat{H}|\sum_{k=1} a_k\psi_k\rangle \\
&= \sum_{j=1} a_j^* \sum_{k=1} a_k \ \langle\psi_j|\hat{H}|\psi_k\rangle \\
&= \sum_{j=1} a_j^* \sum_{k=1} a_k \ E_k \ \cancel{\langle\psi_j|\psi_k\rangle} \rightarrow \delta_{j,k} \\
&= \sum_{j=1} a_j^* a_j \ E_j = \sum_{j=1} |a_j|^2 \ E_j \\
&= |a_1|^2 \ E_1 + |a_2|^2 \ E_2 + \ldots \geq E_1
\end{aligned}
$$

- $\phi \Rightarrow$ Variational function $\Rightarrow$ limit conditions
- $\langle\phi|\hat{H}|\phi\rangle \Rightarrow$ Variational integral

Linear variational function

$$\phi = c_1 f_1 + c_2 f_2 + \cdots + c_n f_n = \sum_{j=1}^{n} c_j f_j \qquad (c_j, f_j \in \Re)$$

$$\langle \phi | \phi \rangle = \langle \sum_{j=1}^{n} c_j f_j | \sum_{k=1}^{n} c_k f_k \rangle = \sum_{j=1}^{n} \sum_{k=1}^{n} c_j c_k \underbrace{\langle f_j | f_k \rangle}_{S_{jk}}$$

$$= \sum_{j=1}^{n} \sum_{k=1}^{n} c_j c_k \; S_{jk}$$

$$\langle \phi | \hat{H} | \phi \rangle = \langle \sum_{j=1}^{n} c_j f_j | \hat{H} | \sum_{k=1}^{n} c_k f_k \rangle = \sum_{j=1}^{n} \sum_{k=1}^{n} c_j c_k \underbrace{\langle f_j | \hat{H} | f_k \rangle}_{H_{jk}}$$

$$= \sum_{j=1}^{n} \sum_{k=1}^{n} c_j c_k \; H_{jk}$$

Linear variational function

- Variational integral $W = \frac{\langle\phi|\hat{H}|\phi\rangle}{\langle\phi|\phi\rangle} = \frac{\sum_{j=1}^{n}\sum_{k=1}^{n} c_j c_k \ H_{jk}}{\sum_{j=1}^{n}\sum_{k=1}^{n} c_j c_k \ S_{jk}}$

$$W \sum_{j=1}^{n}\sum_{k=1}^{n} c_j c_k \ S_{jk} = \sum_{j=1}^{n}\sum_{k=1}^{n} c_j c_k \ H_{jk}$$

$$\begin{cases} W(c_1, c_2, \ldots, c_n) \\ \frac{\partial W}{\partial c_i} = 0, \qquad i = 1, 2, \ldots, n \end{cases}$$

$$\frac{\partial W}{\partial c_i} \sum_{j=1}^{n}\sum_{k=1}^{n} c_j c_k S_{jk} + W \frac{\partial}{\partial c_i} \sum_{j=1}^{n}\sum_{k=1}^{n} c_j c_k S_{jk} = \frac{\partial}{\partial c_i} \sum_{j=1}^{n}\sum_{k=1}^{n} c_j c_k H_{jk}, \qquad i=1,2,\ldots,n$$

Linear variational function

$$\frac{\partial}{\partial c_i}\sum_{j=1}^{n}\sum_{k=1}^{n} c_j c_k S_{jk}=\sum_{j=1}^{n}\sum_{k=1}^{n}\left[\frac{\partial}{\partial c_i}(c_j c_k)\right]S_{jk}=\sum_{j=1}^{n}\sum_{k=1}^{n}\left(c_k\frac{\partial c_j}{\partial c_i}+c_j\frac{\partial c_k}{\partial c_i}\right)S_{jk}$$

- c_j coefficients are independent variables

$$\frac{\partial c_j}{\partial c_i}=0 \quad \text{if } j\neq i, \qquad \frac{\partial c_j}{\partial c_i}=1 \quad \text{if } j=i$$

$$\frac{\partial c_j}{\partial c_i}=\delta_{ij}$$

- Reordering (details can be found in 8th Chapter of *Química Cuántica* by Ira N. Levine)

$$\sum_{k=1}^{n}[(H_{ik}-S_{ik}W)c_k]=0\,, \qquad i=1,2,\ldots,n$$

Linear variational function

- $n = 2$

$$(H_{11} - S_{11}W)c_1 + (H_{12} - S_{12}W)c_2 = 0$$
$$(H_{21} - S_{21}W)c_1 + (H_{22} - S_{22}W)c_2 = 0$$

- n

$$(H_{11} - S_{11}W)c_1 + (H_{12} - S_{12}W)c_2 + \cdots + (H_{1n} - S_{1n}W)c_n = 0$$
$$(H_{21} - S_{21}W)c_1 + (H_{22} - S_{22}W)c_2 + \cdots + (H_{2n} - S_{2n}W)c_n = 0$$
$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots$$
$$(H_{n1} - S_{n1}W)c_1 + (H_{n2} - S_{n2}W)c_2 + \cdots + (H_{nn} - S_{nn}W)c_n = 0$$

- Homogeneous system of equations

Linear variational function

- $n = 2$

$$\begin{vmatrix} H_{11} - S_{11}W & H_{12} - S_{12}W \\ H_{21} - S_{21}W & H_{22} - S_{22}W \end{vmatrix} = 0$$

- n

$$\det(H_{ij} - S_{ij}W) = 0$$

$$\begin{vmatrix} H_{11} - S_{11}W & H_{12} - S_{12}W & \cdots & H_{1n} - S_{1n}W \\ H_{21} - S_{21}W & H_{22} - S_{22}W & \cdots & H_{2n} - S_{2n}W \\ . & . & \cdots & . \\ H_{n1} - S_{n1}W & H_{n2} - S_{n2}W & \cdots & H_{nn} - S_{nn}W \end{vmatrix} = 0$$

- Secular equation $\Rightarrow$ Equation of nth degree in W

Linear variational function

$$W_1 \le W_2 \le \cdots \le W_n$$

$$E_1 \le E_2 \le \cdots \le E_n \le E_{n+1} \le \cdots$$

$$E_1 \le W_1, \quad E_2 \le W_2, \quad E_3 \le W_3, \ldots, \quad E_n \le W_n$$

Definitions

- System Hamiltonian $\Rightarrow \hat{H} \Rightarrow \hat{H}\psi_n = E_n\psi_n$
- Unperturbed Hamiltonian $\Rightarrow \hat{H}^0 \Rightarrow \hat{H}^0\psi_n^{(0)} = E_n^{(0)}\Psi_n^{(0)}$
- Perturbation $\Rightarrow \hat{H}' \Rightarrow \hat{H} = \hat{H}^0 + \hat{H}'$
- Perturbation parameter $\Rightarrow \lambda \Rightarrow \hat{H} = \hat{H}^0 + \lambda\hat{H}'$

$$\lambda \in [0, 1]$$

Non-degenerate perturbation theory

$$\hat{H}\psi_n = (\hat{H}^0 + \lambda \hat{H}')\psi_n = E_n\psi_n \quad \Rightarrow \quad \psi_n = \psi_n(\lambda, q) \quad \text{y} \quad E_n = E_n(\lambda)$$

$$\psi_n = \psi_n|_{\lambda=0} + \left.\frac{\partial \psi_n}{\partial \lambda}\right|_{\lambda=0} \lambda + \left.\frac{\partial^2 \psi_n}{\partial \lambda^2}\right|_{\lambda=0} \frac{\lambda^2}{2!} + \cdots$$

$$E_n = E_n|_{\lambda=0} + \left.\frac{dE_n}{d\lambda}\right|_{\lambda=0} \lambda + \left.\frac{d^2 E_n}{d\lambda^2}\right|_{\lambda=0} \frac{\lambda^2}{2!} + \cdots$$

$$\psi_n|_{\lambda=0} = \psi_n^{(0)} \quad \text{y} \quad E_n|_{\lambda=0} = E_n^{(0)}$$

$$\psi_n^{(k)} = \frac{1}{k!} \left.\frac{\partial^k \psi_n}{\partial \lambda^k}\right|_{\lambda=0}, \qquad E_n^{(k)} = \frac{1}{k!} \left.\frac{d^k E_n}{d\lambda^k}\right|_{\lambda=0}, \qquad k = 1, 2, \ldots$$

Non-degenerate perturbation theory

$$\psi_n = \psi_n^{(0)} + \lambda \psi_n^{(1)} + \lambda^2 \psi_n^{(2)} + \cdots + \lambda^k \psi_n^{(k)} + \cdots$$

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots + \lambda^k E_n^{(k)} + \cdots$$

- Substitution in the Schödinger's equation (details in Section 9.2 of *Química Cuántica* by Ira N. Levine)

$$E_n^{(1)} = \langle \psi_n^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle \qquad \psi_n^{(1)} = \sum_{m \neq n} \frac{\langle \psi_m^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}} \, \psi_m^{(0)}$$

$$E_n^{(2)} = \sum_{m \neq n} \frac{| \langle \psi_m^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle |^2}{E_n^{(0)} - E_m^{(0)}}$$