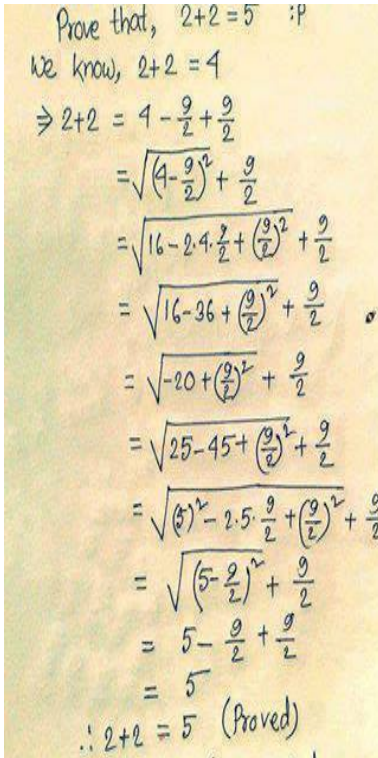


Approximate methods in Quantum Mechanics



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I.A. Variation theorem

I. Variational method



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

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

$$\begin{aligned} \langle \phi | \phi \rangle &= \left\langle \sum_{j=1} a_j \psi_j \middle| \sum_{k=1} a_k \psi_k \right\rangle \\ &= \sum_{j=1} a_j^* \sum_{k=1} a_k \langle \psi_j | \psi_k \rangle \delta_{j,k} \\ &= \sum_{j=1} a_j^* a_j = \sum_{j=1} |a_j|^2 = 1 \end{aligned}$$

I.A. Variation theorem

I. Variational method



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

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

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

$$\begin{aligned} \langle \phi | \phi \rangle &= \left\langle \sum_{j=1}^n c_j f_j \left| \sum_{k=1}^n c_k f_k \right. \right\rangle = \sum_{j=1}^n \sum_{k=1}^n c_j c_k \langle f_j | f_k \rangle \xrightarrow{S_{jk}} \\ &= \sum_{j=1}^n \sum_{k=1}^n c_j c_k S_{jk} \end{aligned}$$

$$\begin{aligned} \langle \phi | \hat{H} | \phi \rangle &= \left\langle \sum_{j=1}^n c_j f_j \left| \hat{H} \right| \sum_{k=1}^n c_k f_k \right\rangle = \sum_{j=1}^n \sum_{k=1}^n c_j c_k \langle f_j | \hat{H} | f_k \rangle \xrightarrow{H_{jk}} \\ &= \sum_{j=1}^n \sum_{k=1}^n c_j c_k H_{jk} \end{aligned}$$

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

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

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

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

$$i=1, 2, \dots, n$$

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

- c_j coefficients are independent variables

$$\frac{\partial c_j}{\partial c_i} = 0 \quad \text{si } j \neq i, \quad \frac{\partial c_j}{\partial c_i} = 1 \quad \text{si } j = i$$
$$\frac{\partial c_j}{\partial c_i} = \delta_{ij}$$

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

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

- $n = 2$

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

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

- n

$$(H_{11} - S_{11}W)c_1 + (H_{12} - S_{12}W)c_2 + \dots + (H_{1n} - S_{1n}W)c_n = 0$$

$$(H_{21} - S_{21}W)c_1 + (H_{22} - S_{22}W)c_2 + \dots + (H_{2n} - S_{2n}W)c_n = 0$$

.....

$$(H_{n1} - S_{n1}W)c_1 + (H_{n2} - S_{n2}W)c_2 + \dots + (H_{nn} - S_{nn}W)c_n = 0$$

- Homogeneous system of equations

- $n = 2$

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

- n

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

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

- Secular equation \Rightarrow Equation of n th degree in W



$$W_1 \leq W_2 \leq \cdots \leq W_n$$

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

$$E_1 \leq W_1, \quad E_2 \leq W_2, \quad E_3 \leq W_3, \dots, \quad E_n \leq W_n$$

II.A. Definitions

II. Perturbation theory

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- 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 $\Rightarrow \lambda \Rightarrow \hat{H} = \hat{H}^0 + \lambda\hat{H}'$

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



II.B. Non-degenerate perturbation theory

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

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

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

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

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



II.B. Non-degenerate perturbation theory

$$\begin{aligned}\Psi_n &= \Psi_n^{(0)} + \lambda \Psi_n^{(1)} + \lambda^2 \Psi_n^{(2)} + \dots + \lambda^k \Psi_n^{(k)} + \dots \\ E_n &= E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots + \lambda^k E_n^{(k)} + \dots\end{aligned}$$

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

$$E_n^{(1)} = \langle \Psi_n^{(0)} | \hat{H}' | \Psi_n^{(0)} \rangle \quad \Psi_n^{(1)} = \sum_{m \neq n} \frac{\langle \Psi_m^{(0)} | \hat{H}' | \Psi_n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}} \Psi_m^{(0)}$$

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