NPTEL ONLINE CERTIFICATION COURSES

NPTEL

Approximate Methods in Quantum Chemistry

Sabyashachi Mishra
Department of Chemistry, IIT Kharagpur

Lecture 07: Variational Principle

Atomic Unit

Symbol	Quantity	Value in a.u.	Value in SI
m_e	Electron mass	1	9.110×10^{-31} kg
e	Electron charge	1	1.602×10^{-19} C
t	Time	1	2.419×10^{-17} s
$\hbar$	$h/2\pi$ (atomic momentum unit)	1	1.055×10^{-34} Js
h	Planck's constant	2π	6.626×10^{-34} Js
a_0	Bohr radius(atomic distance unit)	1	5.292×10^{-11} m
E_H	Hartree (atomic energy unit)	1	4.360×10^{-18} J
c	Speed of light	137.036	2.998×10^{8} m/s
α	Fine structure constant $(= e^2/\hbar c 4\pi\epsilon_0 = 1/c)$	0.00729735	0.00729735
μ_B	Bohr magneton $(= e\hbar/2m_e)$	0.5	9.274×10^{-24} J/T
μ_N	Nuclear magneton	2.723×10^{-4}	5.051×10^{-27} J/T
$4\pi\epsilon_o$	Vacuum permittivity	1	$1.113 \times 10^{-10} C^2/$ Jm
μ_0	Vacuum permeability $(4\pi/c^2)$	6.692×10^{4}	1.257×10^{-6} Ns^2/C^2

NPTEL

Molecular Hamiltonian (in atomic unit)

$$\hat{H} = \sum_{A=1}^{N} -\frac{1}{2M_A}\nabla_A^2 + \sum_{i=1}^{n}\left(-\frac{1}{2}\nabla_i^2 - \sum_{A=1}^{N}\frac{Z_A}{r_{iA}}\right) + \sum_{i=1}^{n}\sum_{j>i}^{n}\frac{1}{r_{ij}} + \sum_{A=1}^{N}\sum_{B>A}^{N}\frac{Z_A Z_B}{R_{AB}}$$

NPTEL

NPTEL ONLINE CERTIFICATION COURSES

NPTEL

Approximate Methods in Quantum Chemistry

Sabyashachi Mishra
Department of Chemistry, IIT Kharagpur

Lecture 08: Variational Principle - II

Variational Principle

$$E_0 = \frac{\langle \psi_0 | \hat{H} | \psi_0 \rangle}{\langle \psi_0 | \psi_0 \rangle}$$

$$E_\phi = \frac{\langle \phi | \hat{H} | \phi \rangle}{\langle \phi | \phi \rangle}$$

$$E_\phi \geq E_0$$

$$\phi \rightarrow \psi_0 \Rightarrow E_\phi \rightarrow E_0$$

Justification:

$$\hat{H}\psi_i = E_i \psi_i$$

$$\phi = \sum_i c_i \psi_i \; ; \; c_i = \langle \psi_i | \phi \rangle$$

$$\langle \hat{H} \rangle = \langle \phi | \hat{H} | \phi \rangle$$

$$= \sum_i |c_i|^2 E_i$$

$$= |c_0|^2 E_0 + |c_1|^2 E_1 + |c_2|^2 E_2 \cdots$$

$$\geq |c_0|^2 E_0 + |c_1|^2 E_0 + |c_2|^2 E_0 \cdots$$

NPTEL

Variational Calculation

$$E_0 = \frac{\langle \psi_0 | \hat{H} | \psi_0 \rangle}{\langle \psi_0 | \psi_0 \rangle}$$

$$E_\phi = \frac{\langle \phi | \hat{H} | \phi \rangle}{\langle \phi | \phi \rangle}$$

$$E_\phi \geq E_0$$

$$\phi \rightarrow \psi_0 \Rightarrow E_\phi \rightarrow E_0$$

Strategy:

$$\phi = \phi(\alpha)$$

$$E_\phi = E_\phi(\alpha)$$

$$\frac{dE_\phi(\alpha)}{d\alpha} = 0$$

$$\phi(\alpha_m); E_\phi(\alpha_m)$$

- Should satisfy boundary conditions
- Should be a well-behaved function

NPTEL

Variational Principle for *Excited States*

$$E_0 = \frac{\langle \psi_0 | \hat{H} | \psi_0 \rangle}{\langle \psi_0 | \psi_0 \rangle}$$

$$E_\phi = \frac{\langle \phi | \hat{H} | \phi \rangle}{\langle \phi | \phi \rangle}$$

$$E_\phi \geq E_0$$

$$\phi \to \psi_0 \Rightarrow E_\phi \to E_0$$

Justification:

$$\phi = \sum_i c_i \psi_i \; ; \; c_i = \langle \psi_i | \phi \rangle$$

Condition : $\langle \psi_0 | \phi \rangle = 0$

$$\begin{aligned}
\langle \hat{H} \rangle &= \langle \phi | \hat{H} | \phi \rangle \\
&= \sum_{i \neq 0} |c_i|^2 E_i \\
&= |c_1|^2 E_1 + |c_2|^2 E_2 + |c_3|^2 E_3 + \cdots \\
&\geq |c_1|^2 E_1 + |c_2|^2 E_1 + |c_3|^2 E_1 \cdots
\end{aligned}$$

NPTEL

NPTEL ONLINE CERTIFICATION COURSES

NPTEL

Approximate Methods in Quantum Chemistry

Sabyashachi Mishra
Department of Chemistry, IIT Kharagpur

Lecture 09: Variational Method: Applications - I

Variational Calculation: Examples

$$\int_0^\infty x^{2n} e^{-ax^2} dx = \frac{(2n)!}{2^{2n+1} n!} \sqrt{\frac{\pi}{a^{2n+1}}}$$

Harmonic Oscillator

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2$$

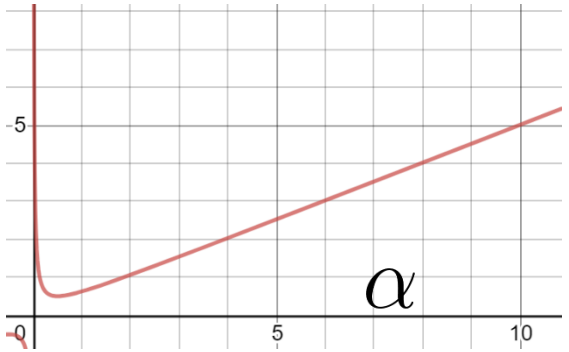
$$\phi_\alpha(x) = e^{-\alpha x^2} \quad (\alpha > 0)$$

$$\langle \phi_\alpha | \phi_\alpha \rangle = \int_{-\infty}^{\infty} e^{-2\alpha x^2}\, dx = \sqrt{\frac{\pi}{2\alpha}}$$

$$\left\langle \hat{H} \right\rangle = \int_{-\infty}^{\infty} dx\; e^{-\alpha x^2} \hat{H}\; e^{-\alpha x^2}$$

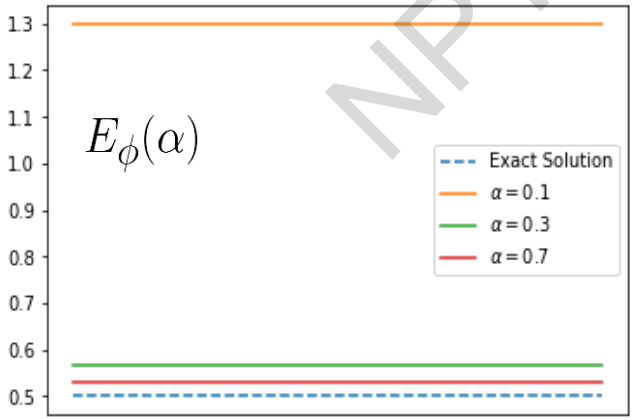
$$= \left(\frac{\hbar^2\alpha}{2m} + \frac{m\omega^2}{8\alpha}\right)\sqrt{\frac{\pi}{2\alpha}}$$

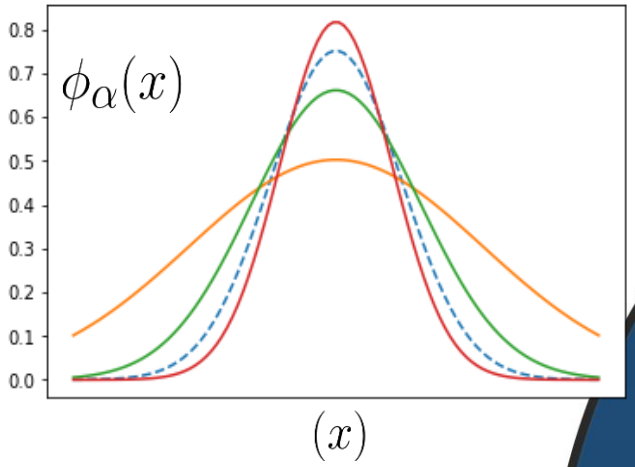
$$E_\phi(\alpha) = \left(\frac{\hbar^2\alpha}{2m} + \frac{m\omega^2}{8\alpha}\right)$$



$$\frac{d}{d\alpha} E_\phi(\alpha) = 0$$

$$\alpha_0 = \frac{m\omega}{2\hbar}$$





Error: 160%, 14%, 6%

NPTEL

Variational Calculation: Examples

Harmonic Oscillator

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2$$

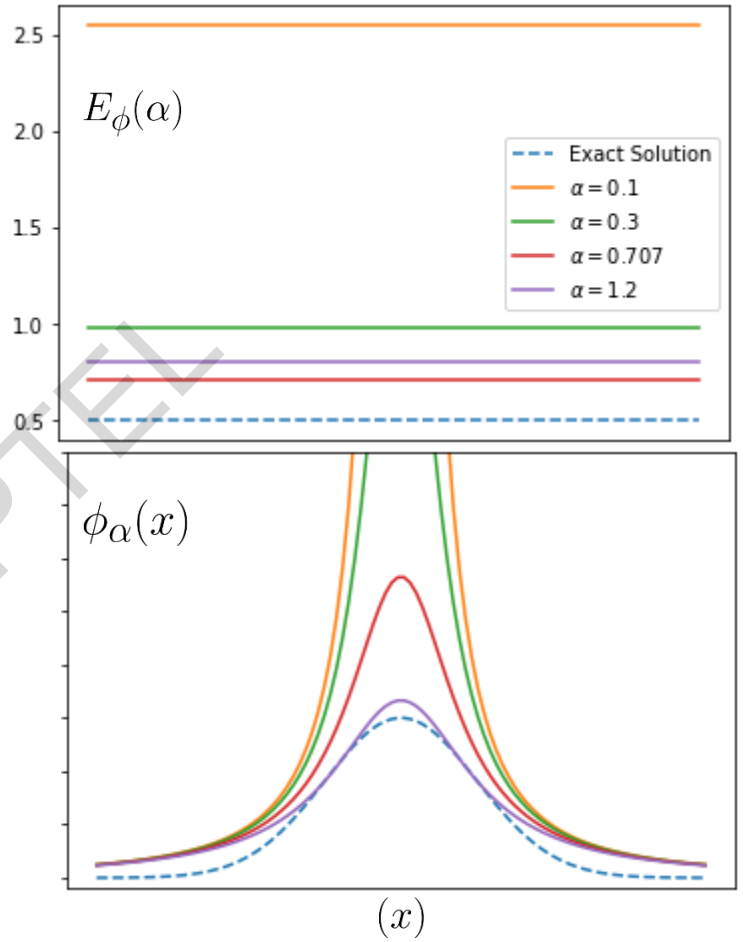
$$\phi_\alpha = \frac{1}{x^2 + \alpha}$$

$$\langle \phi_\alpha | \phi_\alpha \rangle = \int_{-\infty}^{\infty} \frac{1}{(x^2+\alpha)^2}\, dx = \frac{\pi}{2\alpha^{3/2}}$$

$$\left\langle \phi_\alpha \left| \hat{H} \right| \phi_\alpha \right\rangle = \frac{\hbar^2 \pi}{8m\alpha^{5/2}} + \frac{m\omega^2\pi}{4\alpha^{1/2}}$$

$$E_\phi(\alpha) = \frac{\hbar^2}{4m\alpha} + \frac{1}{2}m\omega^2\alpha$$

$$\frac{dE_\phi(\alpha)}{d\alpha} = 0 \qquad \alpha_0 = \frac{1}{\sqrt{2}}\frac{\hbar}{m\omega}$$



Error: 400%, 100%, 40%, 60%

NPTEL

Variational Calculation: Examples

Hydrogen Atom

$$\hat{H} = -\frac{\hbar^2}{2\mu}\left(\frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{1}{r^2\hbar^2}\hat{L}^2\right) - \frac{Ze^2}{4\pi\epsilon_0 r}$$

$$\phi_\alpha = e^{-\alpha r^2}$$

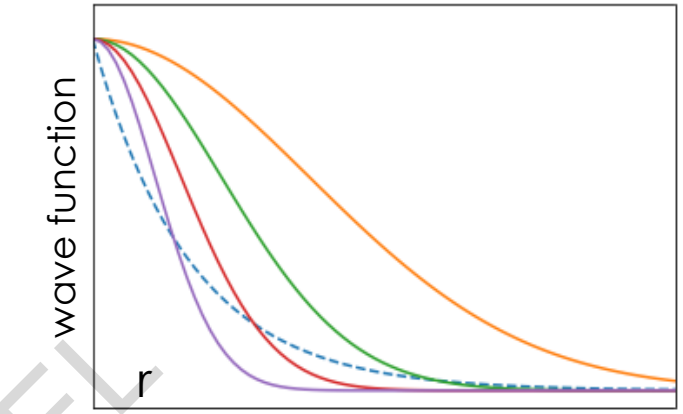
$$\langle\phi_\alpha|\phi_\alpha\rangle = \int_0^\infty e^{-2\alpha r^2} r^2\, dr \int_0^\pi \sin\theta\, d\theta \int_0^{2\pi} d\phi = 4\pi\left(\frac{1}{8\alpha}\sqrt{\frac{\pi}{2\alpha}}\right)$$

$$\left\langle\phi_\alpha\left|\hat{H}\right|\phi_\alpha\right\rangle = 4\pi\left(\frac{3}{16}\sqrt{\frac{\pi}{2\alpha}} - \frac{1}{4\alpha}\right)$$

$$E_\phi(\alpha) = \left(\frac{3\alpha}{2} - \sqrt{\frac{8\alpha}{\pi}}\right)$$

$$\frac{dE_\phi(\alpha)}{d\alpha} = 0 \qquad \alpha_0 = \frac{8}{9\pi}$$

$$E_\phi = -\frac{4}{3\pi} = -0.424 \text{ au}$$



NPTEL

NPTEL ONLINE CERTIFICATION COURSES

NPTEL

Approximate Methods in Quantum Chemistry

Sabyashachi Mishra
Department of Chemistry, IIT Kharagpur

Lecture 10: Linear Variational Method

Variational Principle

- Convergence of energy vs. convergence of wave function
- Experience in choosing trial wave function
- Intuition in choosing trial wave function
- Well suited for ground states

NPTEL

Linear Variational Principle

Let the trial function be, $\phi = c_1\psi_1 + c_2\psi_2$

$$E = \frac{\left\langle \phi \left| \hat{H} \right| \phi \right\rangle}{\langle \phi | \phi \rangle}$$

$$\begin{aligned}\langle \phi | \phi \rangle &= \langle c_1\psi_1 + c_2\psi_2 | c_1\psi_1 + c_2\psi_2 \rangle \\ &= c_1^2 \langle \psi_1 | \psi_1 \rangle + c_2^2 \langle \psi_2 | \psi_2 \rangle + 2c_1c_2 \langle \psi_1 | \psi_2 \rangle\end{aligned}$$

$$\begin{aligned}\left\langle \phi \left| \hat{H} \right| \phi \right\rangle &= \left\langle c_1\psi_1 + c_2\psi_2 \left| \hat{H} \right| c_1\psi_1 + c_2\psi_2 \right\rangle \\ &= c_1^2 \left\langle \psi_1 \left| \hat{H} \right| \psi_1 \right\rangle + c_2^2 \left\langle \psi_2 \left| \hat{H} \right| \psi_2 \right\rangle + 2c_1c_2 \left\langle \psi_1 \left| \hat{H} \right| \psi_2 \right\rangle\end{aligned}$$

NPTEL

Linear Variational Principle

$$E(c_1, c_2) = \frac{c_1^2 H_{11} + c_2^2 H_{22} + 2c_1 c_2 H_{12}}{c_1^2 S_{11} + c_2^2 S_{22} + 2c_1 c_2 S_{12}}$$

$$\frac{\partial E}{\partial c_1} = 0 \Rightarrow c_1(H_{11} - ES_{11}) + c_2(H_{12} - ES_{12}) = 0$$

$$\frac{\partial E}{\partial c_2} = 0 \Rightarrow c_1(H_{12} - ES_{12}) + c_2(H_{22} - ES_{22}) = 0$$

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{12} - ES_{12} & H_{22} - ES_{22} \end{vmatrix} \cdot \begin{vmatrix} c_1 \\ c_2 \end{vmatrix} = 0$$

$$\begin{vmatrix} H_{11} - E & H_{12} \\ H_{12} & H_{22} - E \end{vmatrix} \cdot \begin{vmatrix} c_1 \\ c_2 \end{vmatrix} = 0$$

NPTEL

Linear Variational Principle

When the trial function is,

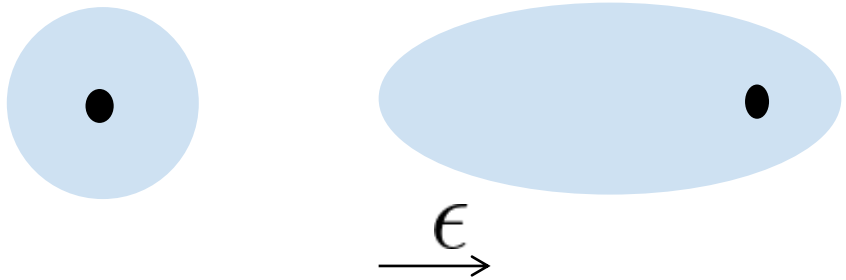
$$\phi = \sum_{i=1}^{n} c_i \psi_i$$

$$\begin{vmatrix} H_{11} - E & H_{12} & \dots & H_{1n} \\ H_{12} & H_{22} - E & \dots & H_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ H_{1n} & H_{2n} & \dots & H_{nn} - E \end{vmatrix} \cdot \begin{vmatrix} c_1 \\ c_2 \\ \vdots \\ c_n \end{vmatrix} = 0$$

NPTEL

Linear Variational Principle: Examples

Polarizability of hydrogen atom



$$\mu = \alpha\epsilon$$

$$\Delta E = -\int_0^{\epsilon} \mu \, d\epsilon' = -\int_0^{\epsilon} \alpha\epsilon' \, d\epsilon' = -\alpha\frac{\epsilon^2}{2}$$

$$\hat{H} = \hat{H}_H - \epsilon r \cos\theta$$

$$\phi = c_1\psi_{1s} + c_2\psi_{2p_z}$$

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{12} - ES_{12} & H_{22} - ES_{22} \end{vmatrix} \cdot \begin{vmatrix} c_1 \\ c_2 \end{vmatrix} = 0$$

NPTEL

NPTEL ONLINE CERTIFICATION COURSES

NPTEL

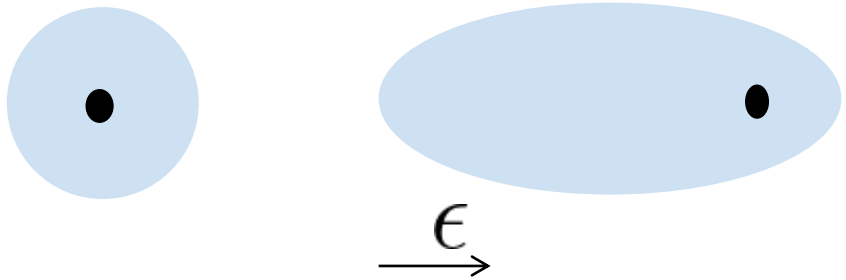
Approximate Methods in Quantum Chemistry

Sabyashachi Mishra
Department of Chemistry, IIT Kharagpur

Lecture 11: Applications of Linear Variational Method

Linear Variational Principle: Examples

Polarizability of hydrogen atom



$$\mu = \alpha\epsilon$$

$$\Delta E = -\int_0^{\epsilon} \mu \, d\epsilon' = -\int_0^{\epsilon} \alpha\epsilon' \, d\epsilon' = -\alpha\frac{\epsilon^2}{2}$$

$$\hat{H} = \hat{H}_H - \epsilon r \cos\theta$$

$$\phi = c_1\psi_{1s} + c_2\psi_{2p_z}$$

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{12} - ES_{12} & H_{22} - ES_{22} \end{vmatrix} \cdot \begin{vmatrix} c_1 \\ c_2 \end{vmatrix} = 0$$

NPTEL

Linear Variational Principle: Examples

$$\int_0^\infty x^n e^{-qx} dx = \frac{n!}{q^{n+1}} \quad q > 0; n > -1$$

Polarizability of hydrogen atom

$$H_{11} = \int \psi_{1s}^* \hat{H}_H \psi_{1s} \, d\tau - \int \psi_{1s}^* \, \epsilon r \cos\theta \, \psi_{1s} \, d\tau = -0.5$$

$$H_{22} = \int \psi_{2p_z}^* \hat{H}_H \psi_{2p_z} \, d\tau - \int \psi_{2p_z}^* \, \epsilon r \cos\theta \, \psi_{2p_z} \, d\tau = -0.5/4$$

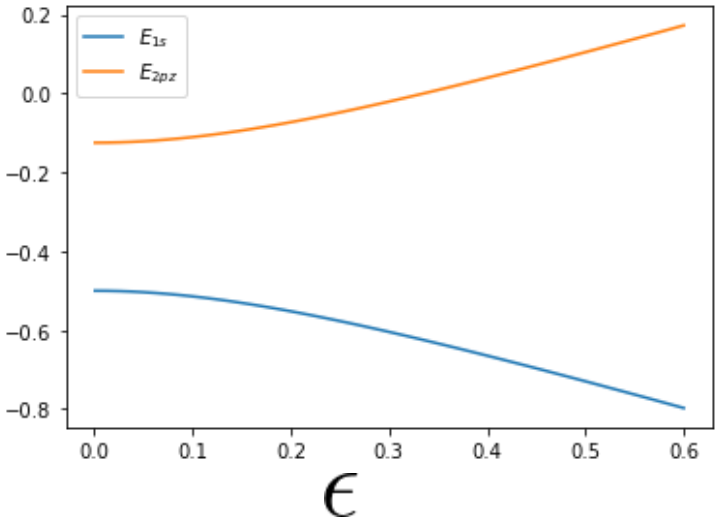
$$H_{12} = \int \psi_{1s}^* \hat{H}_H \psi_{2p_z} \, d\tau - \int \psi_{1s}^* \, \epsilon r \cos\theta \, \psi_{2p_z} \, d\tau = -(\sqrt{2^{15}}/3^5)\epsilon$$

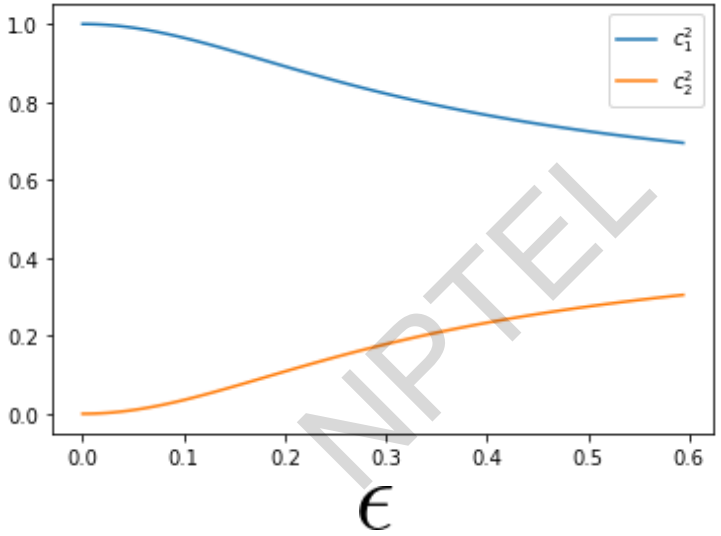
$$\begin{vmatrix} -\frac{1}{2} - E & -(\sqrt{2^{15}}/3^5)\epsilon \\ -(\sqrt{2^{15}}/3^5)\epsilon & -\frac{1}{8} - E \end{vmatrix} \cdot \begin{vmatrix} c_1 \\ c_2 \end{vmatrix} = 0$$

NPTEL

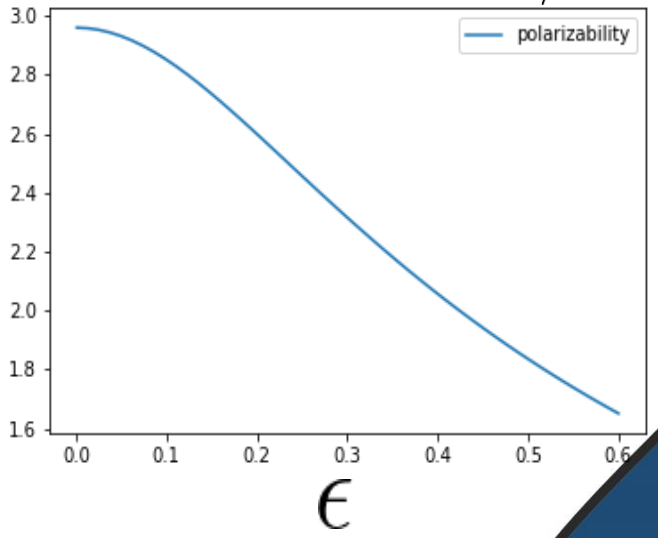
Linear Variational Principle: Examples

Polarizability of hydrogen atom





$$\Delta E = -\alpha\epsilon^2/2$$



NPTEL

Linear Variational Principle in Chemical Bonding

Valence Bond Treatment of H_2

$$\hat{H} = \sum_{A=1}^{2} -\frac{\nabla_A^2}{2M_A} + \sum_{i=1}^{2}\left(-\frac{\nabla_i^2}{2} - \sum_{A=1}^{2}\frac{1}{r_{iA}}\right) + \frac{1}{r_{12}} + \frac{1}{R_{AB}}$$

$$\phi = 1s_A(1)1s_B(2)$$

$$\phi_1 = 1s_A(1)1s_B(2)$$

$$\phi_2 = 1s_A(2)1s_B(1)$$

$$\phi = c_1\phi_1 + c_2\phi_2$$

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{12} - ES_{12} & H_{22} - ES_{22} \end{vmatrix} \cdot \begin{vmatrix} c_1 \\ c_2 \end{vmatrix} = 0$$

NPTEL