

Review Variational Theory and Perturbation Theory

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Variational Theory

Let $\hat{H}|\psi_n\rangle = E_n|\psi_n\rangle$ be the problem you want to solve using variational theory

Now let ψ_{trial} be the approximation to ψ_0

$$E_0 = \frac{\langle \psi_0 | \hat{H} | \psi_0 \rangle}{\langle \psi_0 | \psi_0 \rangle} < E_{\text{trial}} = \frac{\langle \psi_{\text{trial}} | \hat{H} | \psi_{\text{trial}} \rangle}{\langle \psi_{\text{trial}} | \psi_{\text{trial}} \rangle}$$

We can express ψ_{trial} as $|\psi_{\text{trial}}\rangle = \sum_{n=0}^{\infty} C_n |\psi_n\rangle$

$$E_{\text{trial}} = \frac{\langle \psi_{\text{trial}} | \hat{H} | \psi_{\text{trial}} \rangle}{\langle \psi_{\text{trial}} | \psi_{\text{trial}} \rangle} = \frac{\sum_{n=0}^{\infty} C_n^* \left\langle \psi_n \left| \hat{H} \sum_{m=0}^{\infty} C_m |\psi_m\rangle \right. \right\rangle}{\sum_{n=0}^{\infty} C_n^* \left\langle \psi_n \left| \sum_{m=0}^{\infty} C_m |\psi_m\rangle \right. \right\rangle} = \frac{\sum_{n=0}^{\infty} \sum_{m=0}^{\infty} C_n^* C_m \langle \psi_n | \hat{H} | \psi_m \rangle}{\sum_{n=0}^{\infty} \sum_{m=0}^{\infty} C_n^* C_m \langle \psi_n | \psi_m \rangle}$$

Variational Theory 2

$$E_{trial} = \frac{\sum_{n=0}^{\infty} \sum_{m=0}^{\infty} C_n^* C_m E_m \langle \psi_n | | \psi_m \rangle}{\sum_{n=0}^{\infty} \sum_{m=0}^{\infty} C_n^* C_m \langle \psi_n | | \psi_m \rangle} = \frac{\sum_{n=0}^{\infty} C_n^* C_n E_n}{\sum_{n=0}^{\infty} C_n^* C_n}$$

Show that $E_{trial} - E_0$ is zero or positive $E_{trial} - E_0 \geq 0$

Solve the hydrogen atom by Gaussian Function

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

1S $l=0$, using atomic units

$$\hat{H} = \left[-\frac{1}{2r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) - \frac{1}{r} \right]$$

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

using $\psi_{trial} = \text{Exp}(-\alpha r^2)$

Solve for variational minimum of α and obtain the minimum energy. Compare the value with the exact one.

Hint: Gaussian Integrals

$$\langle \psi_{trial} | \hat{H} | \psi_{trial} \rangle = \int_0^{\infty} \exp(-\alpha r^2) \hat{H} \exp(-\alpha r^2) r^2 dr$$

$$\langle \psi_{trial} | \psi_{trial} \rangle = \int_0^{\infty} \exp(-\alpha r^2) \exp(-\alpha r^2) r^2 dr$$

$$\langle r^n \rangle = \int_0^{\infty} r^n \exp(-2\alpha r^2) dr$$

$$\langle r^1 \rangle = \frac{1}{4\alpha}$$

$$\langle r^2 \rangle = \frac{1}{8\alpha} \sqrt{\frac{\pi}{2\alpha}}$$

$$\langle r^4 \rangle = \frac{3}{32\alpha^2} \sqrt{\frac{\pi}{2\alpha}}$$

Morse Oscillator by Perturbation Theory

$$V^{Morse}(x) = D(1 - \exp(-\alpha x))^2 \quad x = R - R_{eq}$$

$$E_n = \left(n + \frac{1}{2}\right) \hbar \omega_e - \left(n + \frac{1}{2}\right)^2 \hbar \omega_e \chi_e$$

$$\omega_e = \alpha \sqrt{\frac{2D}{\mu}}; \quad \omega_e \chi_e = \frac{\alpha^2 \hbar}{2\mu}$$

What is the correction for energy to the Harmonic Oscillator for $n=0$

Expand the Morse potential around $R=R_{eq}$ to obtain the Taylor expansion

$$V^{Morse}(x) = D(1 - \exp(-\alpha x))^2 \approx C_1 x + C_2 x^2 + C_3 x^3 + C_4 x^4 + \dots$$

Find C_1, C_2, C_3, C_4

Morse Oscillator by Perturbation

Obtain the first order correction to the energy using the Harmonic Oscillator as the zeroth order wave function using the third and fourth order term

$$\langle n|x^3|n+3\rangle = \left[\frac{(n+1)(n+2)(n+3)}{8(\omega m / \hbar)^3} \right]^{\frac{1}{2}} \quad \langle n|x^4|n+4\rangle = \frac{1}{4(\omega m / \hbar)^2} [(n+1)(n+2)(n+3)(n+4)]^{\frac{1}{2}}$$

$$\langle n|x^3|n+1\rangle = 3 \left[\frac{(n+1)^3}{8(\omega m / \hbar)^3} \right]^{\frac{1}{2}} \quad \langle n|x^4|n+2\rangle = \frac{1}{2(\omega m / \hbar)^2} (2n+3)[(n+1)(n+2)]^{\frac{1}{2}}$$

$$\langle n-1|x^3|n\rangle = 3 \left[\frac{(n)^3}{8(\omega m / \hbar)^3} \right]^{\frac{1}{2}} \quad \langle n|x^4|n\rangle = \frac{3}{4(\omega m / \hbar)^2} (2n^2 + 2n + 1)$$

$$\langle n-2|x^4|n\rangle = \frac{1}{2(\omega m / \hbar)^2} (2n-1)[(n)(n-1)]^{\frac{1}{2}}$$

$$\langle n-3|x^3|n\rangle = \left[\frac{(n)(n-1)(n-2)}{8(\omega m / \hbar)^3} \right]^{\frac{1}{2}} \quad \langle n-4|x^4|n\rangle = \frac{1}{4(\omega m / \hbar)^2} [(n)(n-1)(n-2)(n-2)]^{\frac{1}{2}}$$

$$\text{else } \langle n|x^3|m\rangle = 0$$

$$\text{else } \langle n|x^4|m\rangle = 0$$

Morse Oscillator by Perturbation

Obtain the second order correction to the energy using the Harmonic Oscillator as the zeroth order wave function using the third order term

$$\langle n|x^3|n+3\rangle = \left[\frac{(n+1)(n+2)(n+3)}{8(\omega m / \hbar)^3} \right]^{\frac{1}{2}}$$

$$\langle n|x^3|n+1\rangle = 3 \left[\frac{(n+1)^3}{8(\omega m / \hbar)^3} \right]^{\frac{1}{2}}$$

$$\langle n-1|x^3|n\rangle = 3 \left[\frac{(n)^3}{8(\omega m / \hbar)^3} \right]^{\frac{1}{2}}$$

$$\langle n-3|x^3|n\rangle = \left[\frac{(n)(n-1)(n-2)}{8(\omega m / \hbar)^3} \right]^{\frac{1}{2}}$$

$$\text{else } \langle n|x^3|m\rangle = 0$$

Perturbation Theory Summary

$$E_n^1 = \langle n^0 | \hat{H}' | n^0 \rangle$$

First order perturbation to energy is expectation value of the perturbation

$$|n^1\rangle = \sum_{k \neq n} \frac{\langle k^0 | (\hat{H}') | n^0 \rangle}{(E_n^{(0)} - E_k^{(0)})} |k^0\rangle$$

First order perturbation to wave function usually mixes the states that are close in energy

$$E_n^2 = \sum_{k \neq n} \frac{|\langle k^0 | \hat{H}' | n^0 \rangle|^2}{(E_n^{(0)} - E_k^{(0)})^2}$$

Second order perturbation to energy is obtained from the first order perturbed wave function

LCAO

For the H_2^+ problem (two hydrogen nuclei are on the z-axis), compared to the LCAO minimal basis method (using only 1S orbitals), why was the decrease in energy not so great when 2S was added. What happens if you add in 2Pz? What happens if you add 2Px? What happens if you add 2Py?

Slater Determinant

Write out the Slater determinant of the four electron system of He_2 in minimal basis set (using 1S orbitals). There are 24 terms. Also explain why the binding energy of He_2 is not as great as H_2

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3, \mathbf{x}_4) = \frac{1}{\sqrt{4!}} \begin{vmatrix} \psi_+(r_1)\alpha(s_1) & \psi_+(r_1)\beta(s_1) & \psi_-(r_1)\alpha(s_1) & \psi_-(r_1)\beta(s_1) \\ \psi_+(r_2)\alpha(s_2) & \psi_+(r_2)\beta(s_2) & \psi_-(r_2)\alpha(s_2) & \psi_-(r_2)\beta(s_2) \\ \psi_+(r_3)\alpha(s_3) & \psi_+(r_3)\beta(s_3) & \psi_-(r_3)\alpha(s_3) & \psi_-(r_3)\beta(s_3) \\ \psi_+(r_4)\alpha(s_4) & \psi_+(r_4)\beta(s_4) & \psi_-(r_4)\alpha(s_4) & \psi_-(r_4)\beta(s_4) \end{vmatrix}$$