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- The Variation Theorem
  - Description
  - Proof
  - Example trial wavefunction for the hydrogenic atom
- The Rayleigh-Ritz Method
  - Description
  - A simple example
  - General description
  - Approximate PIB
- Exercise: Approximation Methods

- This lecture is designed to help you achieve the following learning objectives
  - Describe variation theory and the use of basis sets

The Variation Theorem

Variation Theory

- Exact solutions to Schrodinger's equation are only known in a few systems
- For most chemical systems, we need to use approximation methods
- Many approximation methods are based on the variational principle
- For any test wavefunction Ψ_t, the expectation of the energy is greater than the

ground state energy E_o, $E = \dfrac{\int \Psi_t^* \hat{\mathbf{H}} \Psi_t d\tau}{\int \Psi_t^* \Psi_t d\tau} = \dfrac{\left\langle \Psi_t | \hat{\mathbf{H}} | \Psi_t \right\rangle}{\left\langle \Psi_t | \Psi_t \right\rangle} \geq E_o$

- Approximate wavefunctions can be found by trial and error. They can be tested to see whether they are closer to the true wavefunction.

Proof

- Let $\Psi_t = \sum_n c_n \Psi_n$, where

$$\hat{\mathbf{H}}\Psi_n = E_n \Psi_n.$$

  - *Any* function can be written this way.
  - For simplicity, assume that it is normalized.

- $I = E - E_o$

- $= \int \Psi_t^* (\hat{\mathbf{H}} - E_o) \Psi_t d\tau$

- $= \int \sum_n c_n^* \Psi_n^* (\hat{\mathbf{H}} - E_o) \sum_{n'} c_{n'} \Psi_{n'} d\tau$

- $= \sum_{n,n'} c_n^* c_n' \int \Psi_n^* (\hat{\mathbf{H}} - E_o) \Psi_{n'} d\tau$

- $= \sum_{n,n'} c_n^* c_n' (E_{n'} - E_o) \int \Psi_n^* \Psi_{n'} d\tau$

- $= \sum_n c_n^* c_n (E_n - E_o)$

- Because $c_n^* c_n$ is a square and E_o is the lowest energy, $I \geq 0$. Therefore, $E \geq E_o$.

Example: E_o of a hydrogenic atom

- In this case the true answer is known. Can we use variation theory to find an answer that is close to the true answer?

- Let us use a test function $\Psi_t = e^{-\alpha r^2}$. What is α?

- Remember the Hamiltonian is $\hat{\mathbf{H}} \rightarrow -\dfrac{\hbar^2}{2mr^2}\dfrac{d}{dr}\left(r^2\dfrac{d}{dr}\right) - \dfrac{e^2}{4\pi\epsilon_o r}$. It has no angular dependence.

- Expectation values of the Hamiltonian are Gaussian integrals,

- $\left\langle \Psi_t \,|\, \hat{\mathbf{H}} \,|\, \Psi_t \right\rangle = \dfrac{3\hbar^2\pi^{3/2}}{4\sqrt{2}m_e\sqrt{\alpha}} - \dfrac{e^2}{2\epsilon_o\alpha}$

- $\left\langle \Psi_t \,|\, \Psi_t \right\rangle = \left(\dfrac{\pi}{2\alpha}\right)^{3/2}$

- $E = \dfrac{3\hbar^2\alpha}{2m_e} - \dfrac{e^2\alpha^{1/2}}{\sqrt{2}\epsilon_o\pi^{3/2}}$ is the dependence of energy on α

Example: E_o of a hydrogenic atom

- $E = \dfrac{3\hbar^2\alpha}{2m_e} - \dfrac{e^2\alpha^{1/2}}{\sqrt{2}\epsilon_o\pi^{3/2}}$ is the dependence of energy on α

- How can we find the optimal α?

Checking the variation theorem

- For the hydrogenic atom, $E_o = -\dfrac{m_e e^4}{32\pi^2 \epsilon_o^2 \hbar^2}$.

- For the α that minimizes E,

$$E = \frac{3\hbar^2}{2m_e}\left(\frac{m_e^2 e^4}{18\pi^3 \epsilon_o^3 \hbar^4}\right) - \frac{e^2}{\sqrt{2}\epsilon_o \pi^{3/2}}\left(\frac{m_e e^2}{\sqrt{18}\,\pi^{3/2}\epsilon_o^{3/2}\hbar^2}\right).$$

- $\dfrac{E}{E_o} = \dfrac{32}{12\pi} \approx 0.848$.

- Does this violate the variation theorem?

The Rayleigh-Ritz Method

Optimization with linear algebra

- The variation theorem is $E = \dfrac{\int \Psi_t^* \hat{\mathbf{H}} \Psi_t d\tau}{\int \Psi_t^* \Psi_t d\tau} = \dfrac{\left\langle \Psi_t | \hat{\mathbf{H}} | \Psi_t \right\rangle}{\left\langle \Psi_t | \Psi_t \right\rangle} \geq E_o.$

- Optimizing Ψ_t that depends on many parameters can be challenging

- If we choose a trial function $\phi = \sum c_n f_n$, then choosing c_n is a linear algebra problem, which computers can easily solve

- This is the philosophy behind semi-empirical methods

From linear combinations to matrix elements

- As a simple example, let's choose $\phi = c_1 f_1 + c_2 f_2$. For simplicity, assume that f_n are real.

- $$\int \phi^* \hat{\mathbf{H}} \phi \, d\tau = \int (c_1 f_1 + c_2 f_2) \hat{\mathbf{H}} (c_1 f_1 + c_2 f_2) \, d\tau$$

- $$= c_1^2 \int f_1 \hat{\mathbf{H}} f_1 \, d\tau + c_1 c_2 \int f_1 \hat{\mathbf{H}} f_2 \, d\tau + c_1 c_2 \int f_2 \hat{\,} H f_1 + c_2^2 \int f_2 \hat{\mathbf{H}} f_2$$

- $$= c_1^2 H_{11} + c_1 c_2 H_{12} + c_1 c_2 H_{21} + c_2^2 H_{22}$$

- $= c_1^2 H_{11} + 2 c_1 c_2 H_{12} + c_2^2 H_{22}$ because $\hat{\mathbf{H}}$ is Hermitian

- Similarly, $$\int \phi^* \phi \, d\tau = c_1^2 S_{11} + 2 c_1 c_2 S_{12} + c_2^2 S_{22}$$

- H_{ij} are matrix elements of the Hamiltonian operator and S_{ij} are overlap integrals.

Optimizing the energy

- $E(c_1, c_2) = \dfrac{c_1^2 H_{11} + 2c_1 c_2 H_{12} + c_2^2 H_{22}}{c_1^2 S_{11} + 2c_1 c_2 S_{12} + c_2^2 S_{22}}$ is the energy

- To minimize the energy, we determine the derivative with respect to c_1 as,

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

- By setting this and $\dfrac{\partial E}{\partial c_2}$ equal to zero, we obtain the linear system of equations

  - $c_1(H_{11} - ES_{11}) + c_2(H_{12} - ES_{12}) = 0$
  - $c_1(H_{12} - ES_{12}) + c_2(H_{22} - ES_{22}) = 0$

Matrix Form

- In matrix form, this is $\begin{bmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{12} - ES_{12} & H_{22} - ES_{22} \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix}$

- If $\det |H_{ij} - ES_{ij}| = 0$, this equation has a solution

- This determinant is called a "secular determinant"

The Rayleigh-Ritz Method

- Generalizes the simple example with combining two functions
- The method is to find the linear combination of fixed functions that is closest to the ground-state wavefunction

- $$\Psi_t = \sum_i c_i \Psi_i$$

  - c_i are coefficients, that are allowed to vary
  - Ψ_i are arbitrary functions, not necessarily eigenfunctions of the Hamiltonian operator
- With this form of trial function, linear algebra (instead of multivariate calculus) can be used to optimize Ψ_t

Expectation of energy

- $$E = \frac{\left\langle \Psi_t \,|\, \hat{\mathbf{H}} \,|\, \Psi_t \right\rangle}{\left\langle \Psi_t \,|\, \Psi_t \right\rangle} = \frac{\sum_{i,j} c_i^* c_j \int \Psi_i^* \hat{\mathbf{H}} \Psi_j \, d\tau}{\sum_{i,j} c_i^* c_j \int \Psi_i^* \Psi_j \, d\tau} = \frac{\sum_{i,j} c_i^* c_j H_{ij}}{\sum_{i,j} c_i^* c_j S_{ij}}$$

- H_{ij} is matrix element of the Hamiltonian operator
- S_{ij} is not necessarily a Kronecker delta because Ψ_i are arbitrary, not eigenfunctions of an operator

Minimizing the energy

- $$\delta E = \frac{\sum_{i,j} \delta c_i^* c_j H_{ij}}{\sum_{i,j} c_i^* c_j S_{ij}} - \frac{\left(\sum_{i,j} \delta c_i^* c_j S_{ij} \right) \left(\sum_{i,j} c_i^* c_j H_{ij} \right)}{\left(\sum_{i,j} c_i^* c_j S_{ij} \right)^2}$$

- $$= \frac{\sum_{i,j} \delta c_i^* c_j \left(H_{ij} - E S_{ij} \right)}{\sum_{i,j} c_i^* c_j S_{ij}} = 0 \text{ , using } E = \frac{\sum_{i,j} c_i^* c_j H_{ij}}{\sum_{i,j} c_i^* c_j S_{ij}}$$

- For the minimum E, $\sum_{j} c_j \left(H_{ij} - E S_{ij} \right) = 0$ for every i

- This is a linear algebra problem.
- It has a solution if $\det | H_{ij} - E S_{ij} | = 0$.

Example: Application to PIB

- Let's use the fixed functions $\Psi_1 = x(1-x)$ and $\Psi_2 = x^2(1-x)^2$ in $\Psi_t = c_1 \Psi_1 + c_2 \Psi_2$.
- The matrix elements are,
- $$H_{11} = \frac{\hbar^2}{6m}, \ H_{12} = H_{21} = \frac{\hbar^2}{30m}, \ H_{22} = \frac{\hbar^2}{105m}$$
- $$S_{11} = \frac{1}{30}, \ S_{12} = S_{21} = \frac{1}{140}, \ S_{22} = \frac{1}{630}$$

Approximate PIB energy levels

- $\begin{vmatrix} \dfrac{1}{6} - \dfrac{\epsilon}{30} & \dfrac{1}{30} - \dfrac{\epsilon}{140} \\[2ex] \dfrac{1}{30} - \dfrac{\epsilon}{140} & \dfrac{1}{105} - \dfrac{\epsilon}{630} \end{vmatrix} = (252 - 56\epsilon + \epsilon^2)/529200 = 0$ is the secular

  determinant, where $\epsilon = \dfrac{Em}{\hbar^2}$.

- Using the quadratic equation, $\epsilon = \dfrac{56 \pm \sqrt{2128}}{2} = 51.065$ and 4.93487.

- $E = \dfrac{\hbar^2 \epsilon}{m} = \dfrac{h^2}{m(2\pi)^2} = \dfrac{0.1250018 h^2}{m}$

- $E_{exact} = \dfrac{h^2}{8m} = \dfrac{0.125 h^2}{m}$

Determining coefficients

- The secular equations are,
  - $c_1 \left(H_{11} - ES_{11} \right) + c_2 \left(H_{12} - ES_{12} \right) = 0$
  - $c_1 \left(H_{21} - ES_{21} \right) + c_2 \left(H_{22} - ES_{22} \right) = 0$

- We already have $E = 4.93487 \dfrac{\hbar^2}{m}$. Next, find $\dfrac{c_2}{c_1}$ by rearranging the first

  equation, $\dfrac{c_2}{c_1} = -\dfrac{\left(H_{11} - ES_{11} \right)}{H_{12} - ES_{12}} = -\dfrac{\left(\frac{\hbar^2}{6m} - E/30 \right)}{\left(\frac{\hbar^2}{30m} - E/140 \right)} = 1.13342$

- Thus the unnormalized wavefunction is
  $\Psi = c_1 \left[x(1 - x) + 1.13342 x^2 (x - 1)^2 \right]$

Determining coefficients II

- The unnormalized wavefunction is $\Psi = c_1 \left[x(1-x) + 1.13342x^2(x-1)^2 \right]$

- To normalize, integrate

$$\int_0^1 \Psi^*\Psi \, dx = c_1^2 \int_0^1 \left[x^2(1-x)^2 + 2.26684x^3(1-x)^3 + 1.2864x^4(1-x)^4 \right] dx$$

- Using a standard integral $\int_0^1 x^m(1-x)^n dx = \dfrac{m!\,n!}{(m+n+1)!}$, this is

$$\int_0^1 \Psi^*\Psi \, dx = c_1^2 \left[\frac{2!\,2!}{5!} + 2.26684\frac{3!\,3!}{7!} + 1.2864\frac{4!\,4!}{9!} \right] dx = 0.0515642c_1^2$$

- To normalize, $c_1 = 4.40378$.

- The normalized wave function is $\Psi = 4.40378x(1-x) + 4.99133x^2(x-1)^2$

Exercise: Approximation Methods

https://colab.research.google.com/github/daveminh/Chem550-2024F/blob/main/exercises/02-Approximation_Methods.ipynb

Review Questions

- Compare and contrast perturbation and variation theory

- Does variation theory provide an upper or lower bound to the ground-state energy?

- What is the motivation behind the Raleigh-Ritz method?

- What is a secular determinant?