Variational Principle

often cannot ~~always~~ diagonalize with the full (∞) basis

Hylleraas-Undheim Theorem:

If a hermitian matrix and you sort the matrix from the lowest to the highest diagonal element & truncate to $N\times N$, the eigenvalues λ_i of the truncated matrix are upper limits of the true eigenvalues E_i,

$$E_i \le \lambda_i \quad i = 1 \cdots N$$

λ_1 and λ_2

$$\begin{pmatrix} \boxed{\begin{matrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{matrix}} & \begin{matrix} H_{13} & \cdots \\ H_{23} & \cdots \end{matrix} \\ \begin{matrix} H_{31} & H_{32} \\ \vdots & \vdots \end{matrix} & \begin{matrix} H_{33} & \cdots \\ \vdots & \ddots \end{matrix} \end{pmatrix}$$

E_1, E_2, E_3

$E_1 < \lambda_1,\ E_2 < \lambda_2$

- Prove the special case where we can truncate a 1×1 matrix
  $\hookrightarrow \underline{\underline{H}} = (H_{AA}) = \int d\varphi_A^* \hat{H} \varphi_A$ where φ_A is any basis function

Proof = Let $\hat{H}\psi_n = E\psi_n$ give the true eigenstates ψ_n of $\hat{H}$

Then $\varphi_A = c_1\psi_1 + c_2\psi_2 + \cdots = \sum_n c_n\psi_n$ and $c_{n>1} = 0$ only if $\varphi_1 = \psi_1$

$$\Rightarrow \langle E \rangle = H_{AA} = \langle \varphi_A | \hat{H} | \varphi_A \rangle = \sum_{n,n'} c_n^* c_n \langle \psi_n | \hat{H} | \psi_{n'} \rangle$$

$$= \sum_n c_n^* c_n \langle \psi_n | \hat{H} | \psi_n \rangle$$

$$= \underbrace{\sum_n |c_n|^2 E_n \ge \sum_n |c_n|^2 E_1 \ge E_1}$$

Variational principle: $\langle E \rangle = \langle \varphi | \hat{H} | \varphi \rangle \ge E_1$ = ground state energy

For any choice of function φ

ex. using 'atomic units' where $m_e = 1$, $\hbar = 1$, $\frac{e^2}{4\pi\varepsilon_0} = 1$

H-atom

$$\hat{H}_H = -\frac{1}{2}\nabla_1^2 - \frac{Z}{r_1} = \hat{h}_1(Z=1)$$

$$\varphi_1 = c_1 e^{-Zr_1}\alpha_1$$

$$E = -\frac{1}{2}\text{a.u.} \approx 2.17\times 10^{-18}\text{J}$$

He-atom

$$\hat{H}_{He} = \hat{h}_1(Z=2) + \hat{h}_2(Z=2) + \frac{1}{r_{12}}$$

$$\psi = c^2 e^{-Zr_1} e^{-Zr_2} \frac{1}{\sqrt{2}}(\alpha_1\beta_2 - \alpha_2\beta_1)$$

$\langle E \rangle = ?$ (exp. -2.9 a.u.)

The variation: Let $\psi = c^2 e^{-Z_{eff} r_1} e^{-Z_{eff} r_2} \frac{1}{\sqrt{2}}(\alpha_1\beta_2 - \alpha_2\beta_1)$

$$\langle E \rangle = \langle \psi | \hat{H} | \psi \rangle = Z_{eff}^2 - 2Z Z_{eff} + \frac{5}{8} Z_{eff} \text{ (hook)}$$

if $Z_{eff} = Z \Rightarrow \langle E \rangle = Z^2 - 2Z^2 + \frac{5}{8}Z = 4 - 8 + \frac{5}{4} = -2.75$ a.u.

Can do better. Let $\langle E \rangle = E(Z_{eff})$; the value of Z_{eff} that minimizes $E(Z_{eff})$ gives the lowest $\langle E \rangle$; which is still greater than the real ground state energy

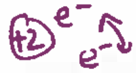
Minimium : $\frac{\partial E(Z_{eff})}{\partial Z_{eff}}$ $2Z_{eff} - 2Z + \frac{5}{8} = 0 \Rightarrow Z_{eff} = Z - \frac{5}{16}$

$= 1.6875$

$\Rightarrow \langle E \rangle_{min} = (1.6875)^2 - 2 \cdot 2 \cdot 1.6875 + \frac{5}{8} \cdot 1.6875$

$= -2.847 \text{ a.u.} \approx -2.90 \text{ a.u.}$

$\approx 1.24 \times 10^{-17}$ J (expt: $1.26 \cdot 10^{-17}$ J)



the e^- shield each other from Z = two attractive charge which appears to each e^- only as $Z_{eff} = 1.6875$

$Z_{eff} = Z - \#\text{inner } e^- - \frac{1}{2}(\#\text{valence } e^- - 1)$

$= 1.5$ for He

motion correlated, lowers E.

$\downarrow$ $e^{-Z_{eff} \cdot r_1} \cdot e^{Z_{eff} r_2}$ not correlated