Tuesday, 8 October 2024 9:56 am

Last time — Variational principle.

To estimate the ground state energy of a Hamiltonian $\hat{H}$.
(lowest energy eigenvalue) E_0

For any state $|\psi\rangle$ in the Hilbert space for $\hat{H}$,

$$\langle\psi|\hat{H}|\psi\rangle \geq E_0$$

(A) Select a 'trial' wavefunction — functional form chosen, vary parameters to minimize $\langle\psi|\hat{H}|\psi\rangle$.

Today — He atom (Tutorial 4)

Trial wavefunction

$$\psi(r_1,r_2) = \psi_{1s}^{Z}(r_1)\,\psi_{1s}^{Z}(r_2)$$

We expect Optimal $Z < 2$
because of shielding/screening from the electrons.
(inter-electron repulsion term in the Hamiltonian).

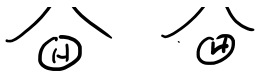
(B) From the variational principle,
we know that when we expand the Hilbert space for the wavefunctions we are considering,
we can continue to minimize $\langle\psi|\hat{H}|\psi\rangle$
and get a better estimate of the ground state energy.

(Context:
We start with a basis that is not complete.)

Eg. Hydrogen molecule.

bonding orbital
(more stable than antibonding orbital)

anti bonding orbital.



anti bonding orbital.

Two-particle spatial wavefunctions

likely to be more stable than AS one

$$\Psi_0^S(\vec{r}_1,\vec{r}_2) = \frac{1}{\sqrt{2}}\left(s_1(\vec{r}_1)s_2(\vec{r}_2) + s_2(\vec{r}_1)s_1(\vec{r}_2)\right)$$

$$\Psi_1^S(\vec{r}_1,\vec{r}_2) = s_1(\vec{r}_1)s_1(\vec{r}_2)$$

$$\Psi_2^S(\vec{r}_1,\vec{r}_2) = s_2(\vec{r}_1)s_2(\vec{r}_2)$$

$$\Psi_3^{AS}(\vec{r}_1,\vec{r}_2) = \frac{1}{\sqrt{2}}\left(s_1(\vec{r}_1)s_2(\vec{r}_2) - s_2(\vec{r}_1)s_1(\vec{r}_2)\right)$$

(Recall: last week
- He atom 1st excited state.

more stable, wavefunction was AS.

Spatial

$\left(\langle|\vec{r}_1-\vec{r}_2|\rangle_{AS} > \langle|\vec{r}_1-\vec{r}_2|\rangle_S\right)$

We work with the spatially symmetric wavefunctions. (Drop S from now)

Let's find $\langle\Psi_0|H|\Psi_0\rangle$.

$$H(\vec{r}_1,\vec{r}_2) = H^{SP}(\vec{r}_1) + H^{SP}(\vec{r}_2) + \frac{e^2}{|\vec{r}_1-\vec{r}_2|}$$

$\vec{r}$: positions of electrons

(Born-Oppenheimer)

H^{SP} - single-particle

$$H^{SP}(\vec{r}) = -\frac{\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{|\vec{r}-\vec{R}_1|} - \frac{e^2}{|\vec{r}-\vec{R}_2|}$$

where $\vec{R}_1$, $\vec{R}_2$ are positions of the nuclei.

Define $\varepsilon = \langle s_1|H^{SP}|s_1\rangle = \langle s_2|H^{SP}|s_2\rangle$

s_1, s_2: s orbitals centered at $\vec{R}_1$ & $\vec{R}_2$.

s orbitals centered at $\vec{R}_1$ & $\vec{R}_2$.

$$\gamma = \langle s_1 | s_2 \rangle \approx 0$$

hopping term $$t = -\langle s_1 | H^{sp} | s_2 \rangle$$

$$\Delta = \langle \psi_0 | \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} | \psi_0 \rangle$$

Then

$$\langle \psi_0 | H | \psi_0 \rangle = 2\varepsilon + \Delta$$

← Variational principle tells us that $2\varepsilon + \Delta \geq E_0$

Work this out:

$$\hat{H}(\vec{r}_1, \vec{r}_2) = \hat{H}^{sp}(\vec{r}_1) + \hat{H}^{sp}(\vec{r}_2) + \frac{e^2}{|\vec{r}_1 - \vec{r}_2|}$$

$\langle s_2 | s_1 \rangle = \langle s_1 | s_2 \rangle \approx 0$

$$\langle \psi_0 | H^{sp} \otimes \mathbb{1}_2 | \psi_0 \rangle$$

$$= \frac{1}{2} \left(\langle s_1| \otimes \langle s_2| + \langle s_2| \otimes \langle s_1| \right)(H^{sp} \otimes \mathbb{1}_2)\left(|s_1\rangle \otimes |s_2\rangle + |s_2\rangle \otimes |s_1\rangle \right)$$

$$= \frac{1}{2} \left(\langle s_1 | H^{sp} | s_1 \rangle \langle s_2 | s_2 \rangle + \langle s_2 | H^{sp} | s_2 \rangle \langle s_1 | s_1 \rangle \right)$$

$$\approx \frac{1}{2}(\varepsilon + \varepsilon) = \varepsilon$$

Similarly $\langle \psi_0 | \mathbb{1}_1 \otimes H^{sp} | \psi_0 \rangle = \varepsilon$

We can do the same for $|\psi_1\rangle$, $|\psi_2\rangle$.

Variational principle: $(2\varepsilon + U) \geq E_0$

$$\langle \psi_1 | H | \psi_1 \rangle = \langle \psi_2 | H | \psi_2 \rangle = 2\varepsilon + U$$

$$U = \langle s_1 s_1 | \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} | s_1 s_1 \rangle = \langle s_2 s_2 | \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} | s_2 s_2 \rangle$$

$|\psi_0\rangle \rightarrow \quad 2\varepsilon + \Delta \geq E_0$

$|\psi_1\rangle, |\psi_2\rangle \rightarrow \quad 2\varepsilon + U \geq E_0$

we expect $U > \Delta$, so $2\varepsilon + U > 2\varepsilon + \Delta$.

So $|\psi_0\rangle$ is a better trial wavefunction than $|\psi_1\rangle$ and $|\psi_2\rangle$.

To get a better estimate for E_0, we can consider linear combinations of $|\psi_0\rangle, |\psi_1\rangle, |\psi_2\rangle$

(Note: $\langle s_1 | s_2 \rangle = 0$ ensures that $|\psi_0\rangle, |\psi_1\rangle, |\psi_2\rangle$ are orthogonal)

Goal: Consider the space $\mathcal{Q}$ spanned by $\{|\psi_0\rangle, |\psi_1\rangle, |\psi_2\rangle\}$.

Find $\min_{|\psi\rangle \in \mathcal{Q}} \langle \psi | H | \psi \rangle$.

One way is to write

$$|\psi\rangle = a_0 |\psi_0\rangle + a_1 |\psi_1\rangle + a_2 |\psi_2\rangle$$

where $\langle \psi | \psi \rangle = 1$.

minimize. (2 variables).

Recall when we discussed the variational principle, we showed that for any $|\psi\rangle$ that H acts on,

(*) $$\langle \psi | H | \psi \rangle = \sum_{n \geq 0} \alpha_n E_n$$

where $\{E_n\}$ are the eigenvalues of H and $\alpha_n \geq 0$

$$\sum_n \alpha_n = 1.$$

(recall $\alpha_n = |c_n|^2$)

$c_n = \langle \psi_n | \psi \rangle$.

We want to find $|\psi\rangle$ such that $\langle \psi | H | \psi \rangle$ is minimum, and find $\min \langle \psi | H | \psi \rangle$

$\min \langle \psi | H | \psi \rangle = E_0$.

Another approach is to find the minimum eigenvalue of H in the subspace $\mathcal{Q}$.

(*) To see this,

let $|\xi_0\rangle, |\xi_1\rangle, |\xi_2\rangle$ be the eigenstates of Π in $\mathcal{U}$.

$$H|\xi_0\rangle = \epsilon_0|\xi_0\rangle$$
$$H|\xi_1\rangle = \epsilon_1|\xi_1\rangle \qquad \epsilon_0 \le \epsilon_1 \le \epsilon_2$$
$$H|\xi_2\rangle = \epsilon_2|\xi_2\rangle$$

were $|\xi_j\rangle = a_0^j|\psi_0\rangle + a_1^j|\psi_1\rangle + a_2^j|\psi_2\rangle$

Then and $|\psi\rangle \in \mathcal{Q}$ can be written as

$$|\psi\rangle = c_0|\xi_0\rangle + c_1|\xi_1\rangle + c_2|\xi_2\rangle \,, \quad \langle\psi|\psi\rangle = 1$$

and $\langle\psi|H|\psi\rangle = |c_0|^2\epsilon_0 + |c_1|^2\epsilon_1 + |c_2|^2\epsilon_2$

$$\geq |c_0|^2\epsilon_0 + |c_1|^2\epsilon_0 + |c_2|^2\epsilon_0$$
$$= \epsilon_0$$

Back to H_2 molecule.

Define matrix A by $A_{ij} = \langle\psi_i|H|\psi_j\rangle$

We know $A_{00} = 2\mathcal{E} + \Delta$, $(\langle\psi_0|H|\psi_0\rangle)$

$$A_{11} = A_{22} = 2\mathcal{E} + U.$$

So far we have:

$$A = \begin{pmatrix} 2\mathcal{E}+\Delta & ? & ? \\ ? & 2\mathcal{E}+U & ? \\ ? & ? & 2\mathcal{E}+U \end{pmatrix}$$

$$A_{01} = \langle\psi_0|H|\psi_1\rangle$$
$$= \frac{1}{\sqrt{2}}\left(\langle s_1 s_2| + \langle s_2 s_1|\right)\left(H^{sp}\otimes\mathbb{1}_2 + \mathbb{1}_1\otimes H^{sp} + \frac{e^2}{|\vec{r}_1 - \vec{r}_2|}\right)\left(|s_1 s_1\rangle\right)$$

$$\approx \frac{1}{\sqrt{2}}\left(\langle s_1|s_1\rangle\langle s_2|H^{sp}|s_1\rangle + \langle s_2|H^{sp}|s_1\rangle\langle s_1|s_1\rangle + 0\right)$$

(assume $\langle \psi_3 | \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} | \psi_1 \rangle \approx 0$)

$= -\sqrt{2}\,t$, where $t = -\langle s_1 | H^{sp} | s_2 \rangle$

assume to be real.

Similarly, $A_{10} = A_{01} = -\sqrt{2}\,t$

$A_{02} = A_{20} = -\sqrt{2}\,t$

assume $\langle \psi_1 | H | \psi_2 \rangle = \langle \psi_2 | H | \psi_1 \rangle \geq 0$

(ψ_1: $s_1 s_1$, ψ_2: $s_2 s_2$)

$$A = \begin{pmatrix} 2\varepsilon + \Delta & -\sqrt{2}t & -\sqrt{2}t \\ -\sqrt{2}t & 2\varepsilon + U & 0 \\ -\sqrt{2}t & 0 & 2\varepsilon + U \end{pmatrix}$$

Diagonalize:

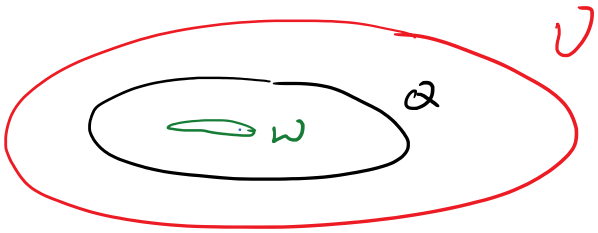
Smallest eigenvalue is

$$E = 2\varepsilon + \frac{1}{2}U - \sqrt{4t^2 + \frac{U^2}{4}}$$

and $E < 2\varepsilon + \Delta$.

This E is the best estimate we have of the true ground state energy for states in Ω.

Let the "actual" Hilbert space for the states of the hydrogen molecule be $\mathcal{V}$.



Let the 1D space spanned by $|\Psi_3\rangle$ be $\mathcal{W}$.

Variational principle

$$\min_{\psi} \langle \psi | H | \psi \rangle$$

$$\min_{\psi \in W} \langle \psi | H | \psi \rangle \geq \min_{\psi \in Q} \langle \psi | H | \psi \rangle \geq \min_{\psi \in V} \langle \psi | H | \psi \rangle$$

$$\min_{\psi \in V} \langle \psi | H | \psi \rangle = \text{true } E_{\text{ground-state}}$$