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1. We are given a solution $\psi(r_1, \dots r_Z)$ to Schrodinger for Z identical particles.

Game plan:

- Construct completly symmetric and antisymetric state ψ_S and ψ_A
- Show both satisfy $\hat{H}\psi = E\psi$
- Show if ψ is symetric under coordinate swap $\psi_A = 0$
- Try w/ example

Since $\hat{H}$ is symetric under particle exchange, permuting coordinates of any eigenfunction ψ will leave energy unchanged.

$$\hat{H}\psi(r_\pi(1), \dots r_\pi(Z)) = E\psi(r_\pi(1), \dots r_\pi(Z)) \quad \dots (1)$$

Let

$$\psi_S(r_1 \dots r_Z) = \frac{1}{Z!}\sum_{\pi \in S_Z} \psi(r_\pi(1), \dots r_\pi(Z)) \quad \dots (2)$$

Symetric permutation in Symetric on Z. ($\pi \in S_Z$)

$$\psi_A(r_1, \dots r_Z) = \frac{1}{Z!}\sum_{\pi \in S_Z} \mathrm{sgn}(\pi)\,\psi(r_{\pi(1)}, \dots r_{\pi(Z)}) \quad \dots (3)$$

Note: Linear combos and degenerate solutions.
ψ_S (2) is fully symmetric
ψ_A (3) is fully antisymmetric
under particle exchange.

Since $\pi \in S_Z$
$\mathrm{sgn}(\pi) = +1$; even
$\mathrm{sgn}(\pi) = -1$; odd.

I cont

but they still satisfy Schrodinger. By linearity and symetry of $\hat{H}$ both remain eigenfunctions

$$\hat{H}\psi_S = E\psi_S \quad ; \quad \hat{H}\psi_A = E\psi_A \quad \dots (4)$$

To look at concrete 2-particle ex: let $\psi(x_1, x_2) = \phi_1(x_1)\phi_2(x_2)$

Where ϕ_1, ϕ_2 are typical orthonormal basis:

Then: $$\psi_S = \frac{1}{\sqrt{2}}\left[\phi_1(x_1)\phi_2(x_2) + \phi_1(x_2)\phi_2(x_1)\right] \quad \dots (5)$$

$$\psi_A = \frac{1}{\sqrt{2}}\left[\phi_1(x)\phi_2(x_2) - \phi_1(x_2)\phi_2(x_1)\right] \quad \dots (6)$$

if $\phi_1 = \phi_2$ then $\psi_A = 0$ [this is literally pauli exclusion principle] ✓

if ψ is already symetric

$\psi(r_1, r_2 \dots) = \psi(r_2, r_1 \dots)$ then antisymetry cancels term by term.

$$\psi(r_1, r_2 \dots) - \psi(r_2, r_1 \dots) = 0 \implies \psi_A = 0 \quad \dots (7)$$

This holds for any antisymetric pair.

Summary:

- ψ_S and ψ_A are constructed from permutation sums of ψ
- Satisfy Schrodinger w/ same energy
- $\psi_A = 0$ if ψ is symetric in <u>any</u> pair.
- This is where antisymetry of slater det for fermions.

2. Extra credit:

Given:

approx Estimates of ground state E_0

- Rayleigh-Ritz Variational: $E_{var} = -27.1$ eV
- 2^{nd} order perturbation thry: $E_{pert} = -26.0$ eV

Q: which estimate is closer to true E_0? if reversed could we Still say which is more accurate?

Variational method:

Guarantees: $E_0 \leq \langle \psi_{trial} | \hat{H} | \psi_{trial} \rangle = E_{var}$ ... (1)

meaning: it provides a strict <u>upper bound</u>. v. true ground state.

We can know this by Expanding any normalized trial in exact Eigenbasis:

$$|\phi\rangle = \sum_n c_n |\psi_n\rangle, \ \sum_n |c_n|^2 = 1 \quad \ldots (2)$$

which yields:

$$E[\phi] = \langle \phi | \hat{H} | \phi \rangle = \sum_n |c_n|^2 E_n \geq E_0 \quad \ldots (3) \ \star$$

so given $E_{var} = -27.1$ eV, we can definitively say

$$E_0 \leq -27.1 \text{ eV} \quad \ldots (4)$$

2 cont.

For Perturbation theory : 2nd order R-S

$$E_{pert} = E_0^{(0)} + E_0^{(1)} + E_0^{(2)} \quad \ldots (5)$$

Where $$E_0^{(2)} = \sum_{n \neq 0} \frac{|\langle n^{(0)} | H' | 0^{(0)} \rangle|^2}{E_0^{(0)} - E_n^{(0)}} < 0 \quad \ldots (6)$$

Since denominator is <0 and numerator >0 ; 2nd order will always lower energy.

But E_{pert} is <u>not guaranteed</u> (unlike variational) to be above or below true E_0. dependent on convergence behavior.
If I recall in class it alway overshot true E_0 ?

SO:

$$E_{var} = -27.1 \text{ eV}, \quad E_{pert} = -26.0 \text{ eV}$$

variational value is lower (more negative), and bc strict/Explicit upper bound we know for certain:

$$\boxed{E_0 \leq E_{var} < E_{pert}} \ldots (7)$$

or

$$\boxed{E_0 \leq -27.1\text{eV} \leq -26.0 \text{ eV} \ldots (8)}$$

E_{var} closer.

Thus perturbation result is further from true energy

and $\boxed{\text{variational estimate is closer to true } E_0 \text{ here}}$

2 - extra credit cont.

But if values were reverse such that

$$: E_{var} = -26.0 \text{ eV}, \quad E_{pert} = -27.1 \text{ eV} \quad \ldots (9)$$

Than we know:

$$E_0 \leq -26.0 \text{ eV}, \quad \text{but } E_{pert} < E_{var} \quad \cdots (10)$$

so here perturbation theory yields lower value than variational upper bound. But we cannot now say if we overshot true value or not.

It remains possible: $E_0 \in [-27.1 \text{ eV}, -26.0] \text{ eV} \cdots (11)$

but without knowing higher order corrections error estimate we cannot definitively say which is closer.

Variational Est. is safer bet (even if on higher side)
while E_{pert} could be closer, or could have overshot.

Summary:

- Varational method mathmatically gaurantees upper bound.
- In first case we can say $E_{vor} = -27.1$ eV is closer to E_0
- In reverse (second case) cannot be confident which is better w/ current info.

$E_0 \leq E_{var}$

Second case: $E_{pert} = -27.1$, $E_{var} = -26.0$ eV

then $E_{pert} < E_0 < E_{var}$ (possible, not guaranteeded)