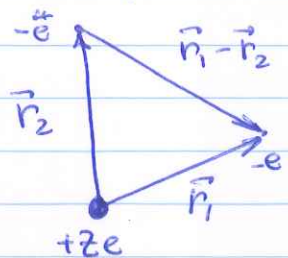# Applications of the variational principle

— Strongly - correlated systems (where e-e interactions are important)

"Simple" example — He atom

$E_{gr} = -78.975 \, eV$
(measured)

Two electron interact with the nucleus and each other

$$\hat{H} = \frac{\hat{P_1}^2}{2m} - \frac{2ke^2}{r_1} + \frac{\hat{P_2}^2}{2m} - \frac{2ke^2}{r_2} + \frac{ke^2}{|\vec{r_1} - \vec{r_2}|}$$

$\hat{H}_0$: two independent electrons

e-e interaction

Can we use perturbation theory — sure...
If we neglect V_{ee} ! $\quad E_{gr}^{(0)} = 2 \times (-Z^2 E_R) = -8 E_R = -109 eV$

Unperturbed wave function: $\quad \psi_0(\vec{r_1}, \vec{r_2}) = \frac{Z^3}{\pi a^3} e^{-Zr_1/a} e^{-Zr_2/a}$

First - order correction: $\quad \Delta E^{(1)} = \langle \psi_0 | \frac{ke^2}{|\vec{r_1} - \vec{r_2}|} | \psi_0 \rangle =$

$$= (ke^2) \left(\frac{Z^3}{\pi a^3} \right)^2 \iint d^3\vec{r_1} d^3\vec{r_2} \, e^{-2Z(r_1 + r_2)/a} \frac{1}{|\vec{r_1} - \vec{r_2}|} = \frac{5}{4} Z E_R$$

{ see calculations in Griffith } ✱

$$\Delta E^{(1)} = \frac{5}{4} Z E_R \overset{Z=2}{=} \frac{5}{2} E_R = 34 \, eV \quad (\text{not } \underline{\text{much}} \text{ so small! } \$)$$

$$E_{gr} \approx -109 \, eV + 34 \, eV = -75 \, eV \quad (\text{overshoot})$$

to get better precision, we need more higher order corrections ... more calculation, ugh!

Can we use the variational method to improve the accuracy? Yes. We can convert "z" into optimisation parameter.

Indeed, each electron's wave function spreads over the nucleus, partially screening its charge

$$\psi_z(\vec{r_1}, \vec{r_2}) = \frac{z^3}{\pi a^3} e^{-zr_1/a} e^{-zr_2/a} = \frac{z^3}{\pi a^3} e^{-z(r_1+r_2)/a}$$

$$\hat{H} = \frac{\hat{P_1}^2}{2m} + \frac{\hat{P_2}^2}{2m} - \frac{2ke^2}{r_1^2} - \frac{2ke^2}{r_2^2} + \frac{ke^2}{|\vec{r_1}-\vec{r_2}|} =$$

$$= \left[\frac{\hat{P_1}^2}{2m} + \frac{\hat{P_2}^2}{2m} - \frac{zke^2}{r_1} - \frac{zke^2}{r_2} \right] + \frac{(z-2)ke^2}{r_1} + \frac{(z-2)ke^2}{r_2} + \frac{ke^2}{|\vec{r_1}-\vec{r_2}|}$$

$$\langle \psi_z | \hat{H} | \psi_z \rangle = 2z^2 E_R + 2(z-2)\left\langle \frac{ke^2}{r_1} \right\rangle + \left\langle \psi_z \left| \frac{ke^2}{|\vec{r_1}-\vec{r_2}|} \right| \psi_z \right\rangle =$$

$$= -2z^2 E_R + 4z(z-2)E_R + \frac{5}{4} E_R = \left(2z^2 - \frac{27}{4} z \right) E_R$$

$$\frac{\partial \langle \psi_z | \hat{H} | \psi_z \rangle}{\partial z} = \left(4z - \frac{27}{4} \right) E_R = 0 \qquad z = \frac{27}{16} \approx 1.69$$

$$E_{gr} \leq \langle \psi_z | \hat{H} | \psi_z \rangle \Big|_{z=\frac{27}{16}} = \left[2 \cdot \left(\frac{27}{16} \right)^2 - 4 \left(\frac{27}{16} \right)^2 \right] E_R = -2 \left(\frac{27}{16} \right)^2 E_R$$

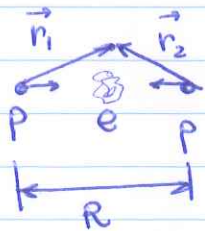$$\underline{E_{gr} \leq -77.5 \text{ eV}}$$

It is in principle improve this result even more by using a more complicated trial function

$$\psi_{\lambda s} (\vec{r_1}, \vec{r_2}) = N e^{-z\lambda(s \max(r_1,r_2) + \min(r_1,r_2))}$$

optimal values: $\lambda = 1.856$, $s = 0.817$

$$\underline{E_{gr} \leq -78.1 \text{ eV}}$$
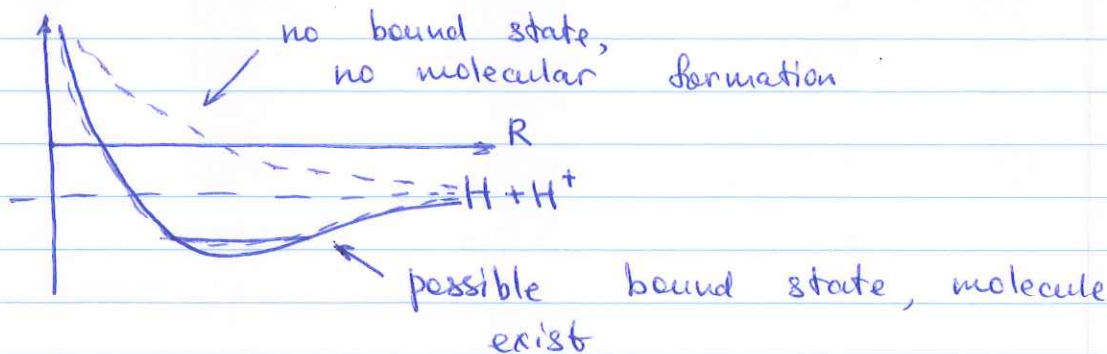
— Molecular structure
"Simple" example — H_2^+ ion

1. Can this system be stable?
(have bound states)

$$\hat{H} = -\frac{\hat{P}^2}{2m} - \frac{ke^2}{r_1} - \frac{ke^2}{r_2} + \frac{ke^2}{R}$$

$p\text{-}p$ repulsion

The main question we are going to answer here is if such ~~be~~ molecule is even possible, i.e. if there is a ground state with the energy lower than $H + H^+$ system

no bound state, no molecular formation

possible bound state, molecule exist

What is a good trial wave function? We expect that an electron will be shared b/w the two protons

$$\psi_+ = A_+ [\psi_0(\vec{r_1}) + \psi_0(\vec{r_2})]$$

where $\psi_0(\vec{r}) = \frac{1}{\sqrt{\pi a^3}} e^{-\tilde{r}/a}$ is the ~~one~~ H-atom ground state wave function

another alternative

$$\psi_- = A_+ [\psi_0(\vec{r_1}) - \psi_0(\vec{r_2})]$$

variational parameter — R, the distance b/w two protons

$A_\pm$ — normalization constants

$$|A_\pm|^2 \int |\psi_0(\vec{r}_1) + \psi_0(\vec{r}_2)|^2 \, d^3\vec{r}_1 \, d^3\vec{r}_2 = 1$$

This value will depend on R as well

$$|A_\pm|^2 = \frac{1}{2\left[1 \pm e^{-R/a}\left(1 + \frac{R}{a} + \frac{1}{3}\left(\frac{R}{a}\right)^2\right)\right]}$$

$$\langle \psi_\pm | \hat{H}_e | \psi_\pm \rangle = |A_\pm|^2 \iint d^3\vec{r}_1 \, d^3\vec{r}_2 \; (\psi_0^*(\vec{r}_1) \pm \psi_0^*(\vec{r}_2)) \times$$

$$\times \left[\frac{\hat{P}^2}{2m} \;\cancel{\;\;}\; - \; \cancel{Ke^2} \; Ke^2\left(\frac{1}{r_1} + \frac{1}{r_2}\right)\right] (\psi_0(\vec{r}_1) \pm \psi_0(\vec{r}_2))$$

$$= \frac{\hat{P}^2 \psi_0(\vec{r}_1)}{2m} - \frac{ke^2}{r_1}\psi_0(\vec{r}_1) \pm \frac{\hat{P}^2 \psi_0(\vec{r}_2)}{2m} \mp \frac{ke^2}{r_2}\psi_0(\vec{r}_2) \mp \frac{ke^2}{r_1}\psi_0(\vec{r}_2) - \frac{ke^2}{r_2}\psi_0(\vec{r}_1)$$

$$= -E_R \psi_0(\vec{r}_1) \pm E_R \psi_0(\vec{r}_2) \mp \frac{ke^2}{r_1}\psi_0(\vec{r}_2) \mp \frac{ke^2}{r_2}\psi_0(\vec{r}_1) =$$

$$= -E_R(\psi_0(\vec{r}_1) \pm \psi_0(\vec{r}_2))$$

$$\langle \psi_\pm | \hat{H}_e | \psi_\pm \rangle = -E_R - 2|A_\pm|^2 ke^2 \left[\langle \psi_0(\vec{r}_1) | \frac{1}{r_2} | \psi_0(\vec{r}_1) \rangle \pm \langle \psi_0(\vec{r}_1) | \frac{1}{r_1} | \psi_0(\vec{r}_2) \rangle \right]$$

$$a\left(\frac{a}{R} - \left(1 + \frac{a}{R}\right)e^{-2R/a}\right) \qquad a\left(1 + \frac{R}{a}\right)e^{-R/a}$$

$$\frac{E_{tot}}{E_R} = \boxed{-1 + \frac{2}{x}\left[\frac{(1+x)e^{-2x} \mp \left(\frac{2}{3}x^2 - 1\right)e^{-x}}{1 \pm (1 + x + x^2/3)e^{-x}}\right].} \qquad x = R/a$$

The graph (with plus sign for comparison) has no minimum, and remains above -1, indicating that the energy is greater than for the proton and atom dissociated. Hence, no evidence of bonding here.

F(x)

H+H⁺