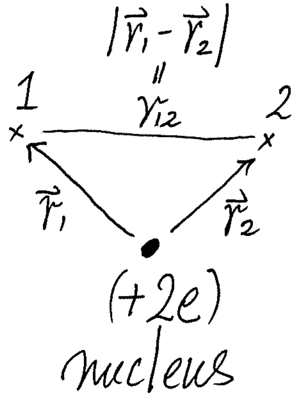
B. Get a sense of the problem: Helium $(Z=2)$ atom



$$\hat{H}_{He} = \underbrace{\left(\frac{-\hbar^2}{2m}\nabla^2_{\vec r_1} - \frac{2e^2}{4\pi\varepsilon_0 r_1}\right)} + \underbrace{\left(\frac{-\hbar^2}{2m}\nabla^2_{\vec r_2} - \frac{2e^2}{4\pi\varepsilon_0 r_2}\right)} + \frac{e^2}{4\pi\varepsilon_0|\vec r_1-\vec r_2|}$$

$$= \hat h_1 + \hat h_2 + \underbrace{\frac{e^2}{4\pi\varepsilon_0|\vec r_1-\vec r_2|}}_{\text{el-el repulsion makes the problem impossible to solve (a real 2-electron problem)}} \quad ☹ \qquad (10)$$

$\hat h_1$, $\hat h_2$: single-particle hydrogen-like hamiltonians ☺

el-el repulsion makes the problem <u>impossible</u> to solve
(a real 2-electron problem)

$$\boxed{\text{Note: } \hat{H}_{He} \text{ is unchanged if we interchange the coordinates of electron 1 and electron 2}}$$

$\hat{H}_{He}\,\psi(\vec r_1,\vec r_2) = E\,\psi(\vec r_1,\vec r_2)$ is the real QM helium atom problem

Formally, $\psi(\vec r_1,\vec r_2)$ is a function of coordinates of both electrons

i.e. $\psi(\vec r_1,\vec r_2) \neq \phi_1(\vec r_1)\cdot\phi_2(\vec r_2)$ [formally NOT True!]

- If (not true!) we ignore el-el interaction term,

Nucleus (+2e) charge

$$\hat{H}_{He} \approx \underbrace{\hat{h}_1 + \hat{h}_2}_{\text{solvable!}} \Rightarrow \text{separable into } \underline{\text{two}} \text{ hydrogen-like } \underline{\text{problems}}$$

Each problem: $\left[-\frac{\hbar^2}{2m}\nabla^2_{\vec{r}} - \frac{2e^2}{4\pi\varepsilon_0 r}\right]\phi_\alpha(\vec{r}) = \varepsilon_\alpha \phi_\alpha(\vec{r})$

[labels solutions]

$$\psi(\vec{r}_1, \vec{r}_2) = \underbrace{\phi_a(1)}_{\substack{\text{electron 1 in}\\ \text{single-electron}\\ \text{state } \phi_a \text{ of energy } \varepsilon_a}} \cdot \underbrace{\phi_b(2)}_{\substack{\text{electron 2 in}\\ \text{single-electron state } \phi_b \text{ of energy } \varepsilon_b}} \qquad (11)^{\dagger}$$

with eigenvalue (energy)

$$E = \varepsilon_a + \varepsilon_b \qquad (12)$$

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† The form in Eq. (11) needs further consideration when we pay attention to the fact that the two electrons are <u>indistinguishable</u> (can't tell which is which) (不可分辨的).

A rough estimation of helium ground state energy (ignoring el-el interaction)

$$\psi_{GS}(\vec{r}_1, \vec{r}_2) = \phi_{GS}(\vec{r}_1)\cdot\phi_{GS}(\vec{r}_2)$$

"Z^2" [nuclear charge is +2e]

[Both e's in ϕ_{GS}]

$$\varepsilon_{GS} = -(2)^2 \underbrace{\frac{me^4}{32\pi^2\varepsilon_0^2\hbar^2}}_{13.6\,eV} = -2\cdot\underbrace{\left(\frac{me^4}{16\pi^2\varepsilon_0^2\hbar^2}\right)}_{27.211\,eV \,\equiv\, 1\text{ Hartree}^{+}\, E_h} = -2E_h$$

$$E_{GS} \overset{(approx)}{=} \varepsilon_{GS} + \varepsilon_{GS} = \underbrace{-4E_h = -108.84\,eV}_{\text{approximate He G.S. energy}}$$

[Actual exp'tal value is $\underbrace{-79\,eV}$ OR $-2.9033\,E_h$]

less stable than rough estimate

-79eV ——— (actual)

[~30eV] ← makes sense because el-el interaction (+ve p.e.) tends to de-stabilize

-108.84eV ------- (ignore el-el interaction)

+ Hartree is an energy unit for measuring energies in atomic units. The hydrogen atom ground state energy is $-\frac{1}{2}$ (in Hartree). See Appendix on Atomic units.

- But the actual problem is $\hat{H}_{He} = \hat{h}_1 + \hat{h}_2 + \underbrace{\frac{e^2}{4\pi\varepsilon_0|\vec{r}_1 - \vec{r}_2|}}_{\text{bad!}}$

Formally, $\underbrace{\psi(\vec{r}_1, \vec{r}_2)}_{\text{2-electron wavefunction}}$, but <u>NOT</u> $\underbrace{\phi_a(\vec{r}_1)\cdot\phi_b(\vec{r}_2)}_{\text{"at best an approximation"}}$ form (Key concept!)

<u>What to do?</u>

- <u>Want</u> to express $\psi(\vec{r}_1, \vec{r}_2)$ as $\underbrace{\phi_a(\vec{r}_1)\cdot\phi_b(\vec{r}_2)}_{\boxed{\text{product of single-particle states}}}$ (<u>an approximation</u>)

<u>Questions</u>

- How to find reasonable approximation to $\phi(\vec{r})$ [single-particle states]?
- How to put the 2 electrons into single-particle states?

- What can be done? [Look at tool box]
  - perturbation
  - Variational Method
  - Hartree & Hartree Fock (mean field) methods

−79eV ——— (actual)

−108.84eV - - - - ($E^{(0)}_{GS}$, unperturbed)

$\updownarrow$ $\underbrace{\sim 30\text{eV}}$ ("perturbation"?)

↑ not small compared with (−108.84eV)

i.e. develop approximations and numerical methods to retain single-particle state picture

Useful to go to Appendix A on the <u>Atomic Units</u>
and return to here

C. Helium Atom Ground State Energy: 1st order Perturbation Theory

- Why? (can be done! Not so for bigger atoms)
- The 1st order integral is important & leads to a switch in idea (and a big idea)

Unperturbed Problem $\rightarrow$ $\hat{H}_0 = \hat{h}_1 + \hat{h}_2$

electron 1 × sees +Ze

electron 2 × sees +Ze

• (+Ze)(Z=2 for Helium)

0th order ↳ But electrons 1 & 2 don't see each other

Ground state?

- Electron 1 in lowest 1s hydrogen-like state
- Electron 2 also in lowest 1s hydrogen-like state

0th order

$$\Psi^{(0)}_{GS}(\vec{r}_1, \vec{r}_2) = \phi_{1s}(\vec{r}_1)\cdot\phi_{1s}(\vec{r}_2) \qquad (13)$$

where

$$\phi_{1s}(\vec{r}) = \left(\frac{Z^3}{\pi a_0^3}\right)^{1/2} e^{-Zr/a_0} \qquad (14)$$

$$E^{(0)}_{GS} = -\frac{Z^2 me^4}{32\pi^2\varepsilon_0^2\hbar^2} - \frac{Z^2 me^4}{32\pi^2\varepsilon_0^2\hbar^2} \qquad (15)$$

- The point is: In doing perturbation, solutions to $\hat{H}_0$ $\underbrace{\text{are known.}}_{\text{Eqs. (13), (14), (15)}}$

- Perturbation Term: Electrons 1 & 2 see each other

$$\hat{H}' = \frac{e^2}{4\pi\varepsilon_0 |\vec{r}_1 - \vec{r}_2|} \qquad (16)$$

1st order shift in energy:

over electrons 1 & 2 coordinates (6 variables)

$$E^{(1)} = \int \psi^{*(0)}_{GS}(\vec{r}_1, \vec{r}_2) \; \hat{H}' \; \psi^{(0)}_{GS}(\vec{r}_1, \vec{r}_2) \, d^3r_1 \, d^3r_2$$

$$\Rightarrow \boxed{E^{(1)} = \iint \underbrace{\phi^*_{1s}(\vec{r}_1)\,\phi^*_{1s}(\vec{r}_2)}_{\text{Eq. (14)}} \frac{e^2}{4\pi\varepsilon_0 |\vec{r}_1 - \vec{r}_2|} \underbrace{\phi_{1s}(\vec{r}_1)\,\phi_{1s}(\vec{r}_2)}_{\text{Eq. (14)}} \, d^3r_1 \, d^3r_2 \qquad (17)}$$

$$= \frac{e^2}{4\pi\varepsilon_0} \frac{Z^6}{\pi^2 a_0^6} \iint e^{-2Zr_1/a_0} \, e^{-2Zr_2/a_0} \frac{1}{|\vec{r}_1 - \vec{r}_2|} \, d^3r_1 \, d^3r_2 \qquad (18) \quad (Z=2)$$

(6 integrals altogether)

In atomic units: $$E^{(1)} = \frac{Z^6}{\pi^2}\iint e^{-2Zr_1}\, e^{-2Zr_2}\, \frac{1}{|\vec{r}_1-\vec{r}_2|}\, d^3r_1\, d^3r_2 \qquad (18')$$

- Key Point is: Integral (18) can be done analytically[+]!

The answer is $$\underset{\nearrow\ \text{do (18)}}{E^{(1)}} = \frac{5}{8}Z\underbrace{\left(\frac{me^4}{16\pi^2\varepsilon_0^2\hbar^2}\right)}_{1\text{ Hartree } E_h} \quad \text{OR} \quad \underset{\uparrow\ \text{do (18')}}{E^{(1)}} = \frac{5}{8}Z \quad \left(\text{Atomic units}\right) \qquad (19)$$

$$\therefore\ \boxed{E \approx \overset{\text{Eq.(13)}\ \swarrow}{E^{(0)}} + \overset{\text{Eq.(17)}\ \downarrow}{E^{(1)}} = \Big(\underset{\uparrow\ 0^{\text{th}}\text{ order}}{-Z^2} + \underset{\uparrow\ 1^{\text{st}}\text{ order}}{\frac{5}{8}Z}\Big)\, E_h} \qquad (20)$$

$Z=2 \Rightarrow$ for helium $$E \approx \underset{\nearrow\ -108.84\text{eV}}{-4} + \underset{\uparrow\ \text{make } E \text{ less negative (el-el interaction de-stabilizes atom)}}{\frac{5}{4}} = -2.75\,(E_h) = -74.83\,\text{eV} \quad (1^{\text{st}}\text{ order approximation})$$

[+] There are several ways to do Eq.(18) integrals. For the moment, focus on the physics!

($-2.75\,E_h$) up to vs ($-2.9033\,E_h$)

- <u>Does it work?</u> $-74.83\,\text{eV}$ (1st order) <u>vs</u> $-79\,\text{eV}$ (exp'tal, "exact")

↖ • Not bad! ↗

$E^{(0)}_{GS} + E^{(1)}_{GS}$ - - - - - ($-74.83\,\text{eV}$) (1st order perturbation)

—— actual ($-79\,\text{eV}$)

$E^{(0)}_{GS}$ - - - - - ($-108.84\,\text{eV}$)

$\boxed{\text{• Why 1st order result > True GS energy?}}$

Must be! ($\because$ $\underbrace{\text{Variational Principle!}}$)

Up to 1st order is the same as taking Eq.(13) (with Eq.(14)) as a trial wavefunction, thus result ($-74.83\,\text{eV}$) must be higher than the true G.S. energy ($-79\,\text{eV}$).

<u>Why bother with all these?</u>

Eq.(17) (and result Eq.(20)) leads to important <u>ideas</u>

Variational Method: An exercise

- $$\hat{H}_{helium} = \frac{-\hbar^2}{2m}\nabla^2_{\vec{r}_1} - \frac{2e^2}{4\pi\varepsilon_0 r_1} - \frac{\hbar^2}{2m}\nabla^2_{\vec{r}_2} - \frac{2e^2}{4\pi\varepsilon_0 r_2} + \frac{e^2}{4\pi\varepsilon_0|\vec{r}_1-\vec{r}_2|} \qquad (10)$$

- Start with Eq.(13) & Eq.(14): $$\psi^{trial}_{GS}(\vec{r}_1, \vec{r}_2) = \frac{Z^3}{\pi a_0^3} e^{-\frac{Z r_1}{a_0}} e^{-\frac{Z r_2}{a_0}} \qquad (21)$$

  Instead of fixing $Z=2$, take Z as variation parameter

  then $\langle \hat{H}_{helium} \rangle = Z^2 - \frac{27}{8} Z$ (Hartree) (Ex.)

  Best value of Z? $\frac{\partial \langle \hat{H}_{helium} \rangle}{\partial Z} = 0 \Rightarrow Z^* = \frac{27}{16} = 1.6875$

  Best estimate $E_{GS} = -2.8477\, E_h$ (c.f. $-2.9033\, E_h$ exp't)

Picture: Due to the presence of another electron, it looks as if an electron sees an effective $Z^* = 1.6875e$ from the nucleus. "Screening effect"!

Hinting at a big idea

- Eq.(10) has $\underbrace{\text{el-el term}}_{\text{[real 2-particle problem]}}$, but Eq.(21) treated it as if it is an effective single-particle problem, but the nuclear charge becomes $+Z^{*}e$ (or $+Z_{eff}\,e$)

- It looks like $$V(r) = \frac{\overset{\text{[attractive]}}{+2e^2}}{4\pi\varepsilon_0 r} + [\text{ rough effect due to } \underbrace{\text{other electron}}_{\text{[repulsive]}}]$$ $$\approx \frac{Z_{eff}\,e^2}{4\pi\varepsilon_0 r} \qquad (Z_{eff} \neq 2\ (<2)) \quad \text{(makes sense)}$$

Big idea: Nuclear attraction and rough (averaged) effect of other electrons may be modelled by an effective single-particle $V^{(eff)}(r)$! (22)

∴ Variational Calculation using ψ_{GS}^{trial} (Eq.(21)) as trial wavefunction supports the ideas of...

- reducing problem to single-electron problem
- single electron feels an effective $V^{(eff)}(r)$ that includes nuclear charge <u>AND</u> the effects of the other electron approximately.

Physical Picture of Integral Eq.(17) due to electron-electron interaction

Eq.(17):
$$J_{1s,1s} = \iint \phi^*_{1s}(\vec{r}_1)\,\phi^*_{1s}(\vec{r}_2)\,\frac{e^2}{4\pi\varepsilon_0|\vec{r}_1-\vec{r}_2|}\,\phi_{1s}(\vec{r}_1)\,\phi_{1s}(\vec{r}_2)\,d^3r_1\,d^3r_2 \qquad (17)$$

[call it J]

$$= \iint \frac{\left(-e\left|\phi_{1s}(\vec{r}_1)\right|^2\right)\left(-e\left|\phi_{1s}(\vec{r}_2)\right|^2\right)}{4\pi\varepsilon_0|\vec{r}_1-\vec{r}_2|}\,d^3r_1\,d^3r_2$$

$$= \iint \frac{\rho_{1s}(\vec{r}_1)\,d^3r_1\cdot\rho_{1s}(\vec{r}_2)\,d^3r_2}{4\pi\varepsilon_0|\vec{r}_1-\vec{r}_2|}$$

looks very E&M like!

$$\overbrace{\sim\frac{Q_1Q_2}{4\pi\varepsilon_0|\vec{r}_1-\vec{r}_2|}\ \text{\& add up all contributions}}$$

$$\rho_{1s}(\vec{r}_1) \equiv \underbrace{-e}\,\underbrace{\left|\phi_{1s}(\vec{r}_1)\right|^2} \quad\Rightarrow\quad \underbrace{\rho_{1s}(\vec{r}_1)\,d^3r_1}$$

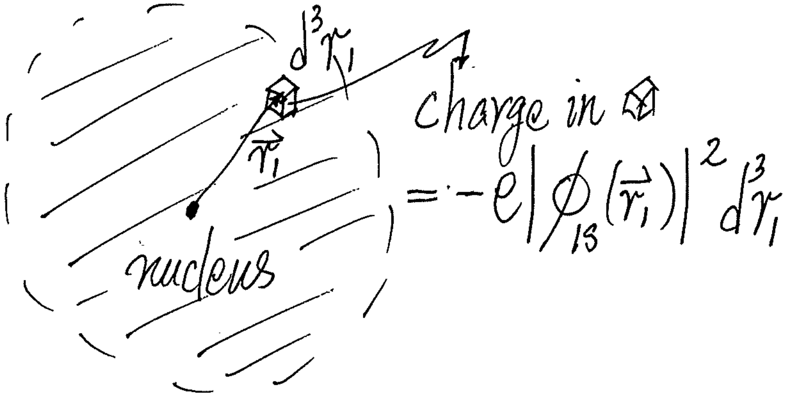
(similar interpretation for $\rho_{1s}(\vec{r}_2)\,d^3r_2$)

charge density at $\vec{r}_1$ due to electron 1

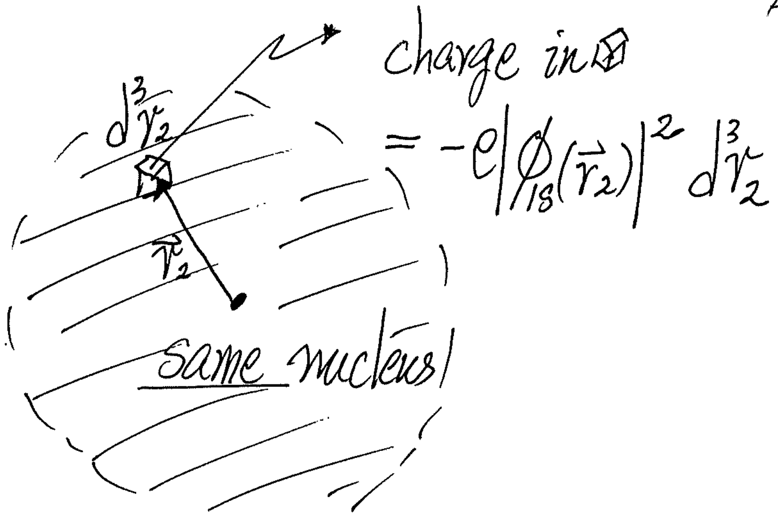
charge of electron

prob. density of finding electron 1 at $\vec{r}_1$ (if it is in a state called ϕ_{1s})

charge in volume element d^3r_1 at $\vec{r}_1$ due to electron 1



Electron 1 in state ϕ_{1s}



Electron 2 in state ϕ_{1s}

- Coulomb interaction between patches of charge

$$= \frac{\left(-e|\phi_{1s}(\vec{r}_1)|^2 d^3r_1\right)\left(-e|\phi_{1s}(\vec{r}_2)|^2 d^3r_2\right)}{4\pi\varepsilon_0 |\vec{r}_1 - \vec{r}_2|}$$

- Total el-el interaction energy (adding up all contributions)

$$= \iint \frac{\left(-e|\phi_{1s}(\vec{r}_1)|^2\right)\left(-e|\phi_{1s}(\vec{r}_2)|^2\right)}{4\pi\varepsilon_0 |\vec{r}_1 - \vec{r}_2|} d^3r_1\, d^3r_2 \quad \text{(which is Eq. (17))}$$

- Interpretation of Eq.(17) doesn't depend on explicit form of $\phi_{1s}(\vec{r}_1)$
- Work for any state $\phi(\vec{r}_1)$
- Can generalize to one electron in some state $\phi_A(\vec{r}_1)$ [say electron 1] and another electron [say electron 2] in some state $\phi_B(\vec{r}_2)$
  [ϕ_A, ϕ_B may or may not be the same state]

$$\boxed{J_{AB} = \iint \phi_A^*(\vec{r}_1)\, \phi_B^*(\vec{r}_2)\, \frac{e^2}{4\pi\varepsilon_0 |\vec{r}_1 - \vec{r}_2|}\, \phi_A(\vec{r}_1)\, \phi_B(\vec{r}_2)\, d^3r_1\, d^3r_2 \qquad (23)}$$

- Called "Coulomb integral" or "Direct Coulomb integral"
- Has (classical) E&M interpretation
- Is there an "indirect Coulomb integral"?

Back to Eq. (17) OR (23): 1st order result is indicative

$$\int -e\,\phi_{1s}^*(\vec{r}_1)\underbrace{\left(\int \frac{-e\,|\phi_{1s}(\vec{r}_2)|^2\,d^3r_2}{4\pi\varepsilon_0\,|\vec{r}_1-\vec{r}_2|}\right)}_{}\phi_{1s}(\vec{r}_1)\,d^3r_1$$

- Electric Potential due to electron 2 at location $\vec{r}_1$
- function of $\vec{r}_1$ (integrated over $\vec{r}_2$)

$$= \int \phi_{1s}^*(\vec{r}_1)\underbrace{\left(\int \frac{+e^2\,|\phi_{1s}(\vec{r}_2)|^2\,d^3r_2}{4\pi\varepsilon_0\,|\vec{r}_1-\vec{r}_2|}\right)}_{}\phi_{1s}(\vec{r}_1)\,d^3r_1$$

Mathematical form

$$\int \phi_{1s}^*(\vec{r}_1)\underbrace{\hat{V}^{(eff)}_{el\text{-}el}(\vec{r}_1)}_{}\phi_{1s}(\vec{r}_1)\,d^3r_1$$

an effective p.e. term due to another electron

potential energy of a charge (−e) at $\vec{r}_1$ due to electron 2 in some state ϕ_{1s}

$$= \int \phi_{1s}^*(\vec{r}_1)\;V^{(eff)}_{el\text{-}el}(\vec{r}_1)\;\phi_{1s}(\vec{r}_1)\,d^3r_1$$

- Suggesting that other electrons may be treated approximately as an effective potential.

Or for $\phi_A(\vec{r}_1)\,\phi_B(\vec{r}_2)$,

$$\int \phi_A^*(\vec{r}_1)\left(\int \frac{e^2\,|\phi_B(\vec{r}_2)|^2\,d^3r_2}{4\pi\varepsilon_0|\vec{r}_1-\vec{r}_2|}\right)\phi_A(\vec{r}_1)\,d^3r_1 \qquad (24)$$

- It is like electron 1 sees an effective potential energy function $V_{el\text{-}el}^{eff}(\vec{r}_1)$ due to the other electron (electron 2) in addition to the nuclear attraction
- Again, it supports the ideas of reducing problem to single-electron problem by (working out) an effective potential energy term
- Eq. (24) is important in developing the <u>Hartree approximation</u> (a powerful method).