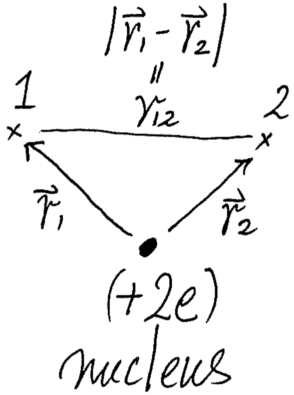
B. Get a sense of the problem: Helium ($Z=2$) atom



$$\hat H_{He} = \underbrace{\left(\frac{-\hbar^2}{2m}\nabla^2_{\vec r_1} - \frac{2e^2}{4\pi\varepsilon_0 r_1}\right)} + \underbrace{\left(\frac{-\hbar^2}{2m}\nabla^2_{\vec r_2} - \frac{2e^2}{4\pi\varepsilon_0 r_2}\right)} + \frac{e^2}{4\pi\varepsilon_0|\vec r_1-\vec r_2|} \tag{8}$$

$$= \hat h_1 + \hat h_2 + \underbrace{\frac{e^2}{4\pi\varepsilon_0|\vec r_1-\vec r_2|}}$$

☹

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

☺

el-el repulsion makes the problem impossible to solve
(a real 2-electron problem)

Note: $\hat H_{He}$ 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,

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

Nucleus (+2e) charge

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

$\underbrace{\text{[labels solutions]}}_{\text{known!}}$

$$\psi(\vec{r}_1, \vec{r}_2) = \underbrace{\phi_a(1)}_{\substack{\text{electron 1 in} \\ \text{single-electron} \\ \text{state } \phi_a \text{ of energy } \varepsilon_a}} \cdot \underbrace{\phi_b(2)}_{\substack{\text{electron 2 in} \\ \text{single-electron state } \phi_b \text{ of energy } \varepsilon_b}} \qquad (9)^{\dagger}$$

with eigenvalue (energy)

$$E = \varepsilon_a + \varepsilon_b \qquad (10)$$

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† The form in Eq. (9) needs further consideration when we pay attention to the fact that the two electrons are indistinguishable (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 $+2e$]

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

defines Hartree

[Both e's in ϕ_{GS}]

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

[Actual exp'tal value is $\underbrace{-79\,\text{eV}}$ 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)

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† 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 NOT $\underbrace{\phi_a(\vec{r}_1)\cdot\phi_b(\vec{r}_2)}_{\text{"at best an approximation"}}$ form (Key concept!)

What to do?

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

Questions

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

Do Better for GS energy? [Look at tool box]

-79eV —— (actual)

-108.84eV ---- ($E_{GS}^{(0)}$, unperturbed)

~30eV ("perturbation"?)

not small compared with (-108.84eV)

- perturbation
- Variational Method
- Hartree & Hartree Fock (mean field) methods

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

Approximate interacting particles as if they are independent

"Independent-Particle Approximation"

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

C. Helium Atom Ground State Energy: 1^{st} order Perturbation Theory and More

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

Unperturbed Problem →

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

electron 1 sees +Ze

electron 2 sees +Ze

(+Ze)(Z=2 for Helium)

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

[no interaction term]

Ground state (unperturbed)

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

0th order

$$\psi^{(0)}_{GS}(\vec{r}_1, \vec{r}_2) = \phi_{1s}(\vec{r}_1) \cdot \phi_{1s}(\vec{r}_2) \qquad (11)$$

where

$$\phi_{1s}(\vec{r}) = \left(\frac{Z^3}{\pi a_0^3}\right)^{1/2} e^{-Zr/a_0} \qquad (12)$$

$$E^{(0)}_{GS} = -\frac{Z^2 me^4}{32\pi^2\varepsilon_0^2\hbar^2} - \frac{Z^2 me^4}{32\pi^2\varepsilon_0^2\hbar^2} \qquad (13)$$

(Z=2) [-108.84eV]

- The point is: In doing perturbation, solutions to $\hat{H}_0$ $\underbrace{\text{are known.}}_{\text{Eqs. (11), (12), (13)}}$

- Perturbation Term: <u>Electrons 1 & 2 see each other</u>

$$\hat{H}' = \frac{e^2}{4\pi\varepsilon_0 |\vec{r}_1 - \vec{r}_2|} \qquad (14)$$

<u>1st order shift in energy:</u>

$$E^{(1)} = \int \psi^{*(0)}_{GS}(\vec{r}_1, \vec{r}_2)\ \hat{H}'\ \psi^{(0)}_{GS}(\vec{r}_1, \vec{r}_2)\ \overbrace{d^3r_1\, d^3r_2}^{\text{over electrons 1 \& 2 coordinates (6 variables)}}$$

$$\Rightarrow \boxed{E^{(1)} = \iint \underbrace{\phi^*_{1s}(\vec{r}_1)\ \phi^*_{1s}(\vec{r}_2)}_{\text{Eq. (12)}}\ \frac{e^2}{4\pi\varepsilon_0|\vec{r}_1 - \vec{r}_2|}\ \underbrace{\phi_{1s}(\vec{r}_1)\ \phi_{1s}(\vec{r}_2)}_{\text{Eq. (12)}}\ d^3r_1\, d^3r_2 \qquad (15)}$$

$$= \frac{e^2}{4\pi\varepsilon_0}\frac{Z^6}{\pi^2 a_0^6}\iint e^{-2Zr_1/a_0}\, e^{-2Zr_2/a_0}\, \frac{1}{|\vec{r}_1 - \vec{r}_2|}\, d^3r_1\, d^3r_2 \qquad (16) \qquad (Z=2)$$

(6 integrals altogether)

In atomic units: $$E^{(1)} = \frac{Z^6}{\pi^2}\iint e^{-2Zr_1}\, e^{-2Zr_2}\, \frac{1}{|\vec{r}_1-\vec{r}_2|}\, d^3r_1\, d^3r_2 \qquad (16')$$

- Key Point is: Integral (16) can be done analytically[+]!

The answer is $$\underset{\text{do (16)}}{E^{(1)}} = \frac{5}{8}Z\underbrace{\left(\frac{me^4}{16\pi^2\varepsilon_0^2\hbar^2}\right)}_{1\text{ Hartree } E_h} \quad \text{OR} \quad \underset{\text{do(16')}}{E^{(1)}} = \frac{5}{8}Z \quad \left(\text{atomic units}\right) \qquad (17)$$

$$\therefore \boxed{E \approx \overset{\text{Eq.(13)}}{E^{(0)}} + \overset{\text{Eq.(17)}}{E^{(1)}} = \Big(\underset{0^{th}\text{ order}}{-Z^2} + \underset{1^{st}\text{ order}}{\frac{5}{8}Z}\Big)\, E_h} \qquad (19)$$

$Z=2 \Rightarrow$ for helium $$E \approx \underset{-108.84\,\text{eV}}{-4} + \underset{\text{make } E \text{ less negative (el-el interaction de-stabilizes atom)}}{\frac{5}{4}} = -2.75\,(E_h) = -74.83\,\text{eV} \quad (1^{st}\text{ order approximation}) \qquad (20)$$

[+] There are several ways to do Eq.(16) integrals. For the moment, focus on the physics!

Does it work?

Actual E_{GS} (-79eV) $(-2.9033\,E_h)$

(-74.83eV) $(-2.75\,E_h)$ ---- $E^{(0)}_{GS} + E^{(1)}_{GS}$ (up to 1st order)

Not Bad!

(-108.84eV) $(-4\,E_h)$ ------ $E^{(0)}_{GS}$ (0th order)

Implications

- Expressing $\psi_{GS}(\vec{r}_1, \vec{r}_2) \approx \underbrace{\phi_{1s}(\vec{r}_1) \cdot \phi_{1s}(\vec{r}_2)}_{\text{product of single-particle states}}$ may be an approximation that works!

  two-particle state

- Variational Method viewpoint

  Take $$\psi^{(\text{trial})}_{GS}(\vec{r}_1, \vec{r}_2) = \left(\frac{Z^3}{\pi a_0^3}\right)^{1/2} e^{-\frac{Zr_1}{a_0}} \cdot \left(\frac{Z^3}{\pi a_0^3}\right)^{1/2} e^{-\frac{Zr_2}{a_0}}$$ with $Z=2$ as Trial Wavefunction

  [it is a trial wavefunction without a variation parameter]

  $$\text{Eq.(20)} \Rightarrow \langle \hat{H}_{He} \rangle_{\psi^{(\text{trial})}_{GS}} = -2.75\,E_h = -74.83\,\text{eV} > E^{(\text{actual})}_{GS}$$

This viewpoint leads to important ideas!

Variational Method: An exercise

- $$\hat{H}_{helium} = \frac{-\hbar^2}{2m}\nabla^2_{\vec{r}_1} - \frac{2e^2}{4\pi\varepsilon_0 r_1} - \frac{\hbar^2}{2m}\nabla^2_{\vec{r}_2} - \frac{2e^2}{4\pi\varepsilon_0 r_2} + \frac{e^2}{4\pi\varepsilon_0|\vec{r}_1-\vec{r}_2|} \qquad (8)$$

- Start with Eq.(11) & Eq.(12): $\psi^{trial}_{GS}(\vec{r}_1, \vec{r}_2) = \frac{Z^3}{\pi a_0^3} e^{-\frac{Zr_1}{a_0}} e^{-\frac{Zr_2}{a_0}}$ (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.(8) 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 $$V(r) = \frac{\overset{\text{[attractive]}}{+2}e^2}{4\pi\varepsilon_0 r} + \left[\text{rough effect } \underbrace{\text{due to other electron}}_{\text{[repulsive]}}\right]$$
$$\approx \frac{Z_{eff}\, e^2}{4\pi\varepsilon_0 r} \qquad (Z_{eff} \neq 2\ (<2)) \quad \text{(makes sense)}$$

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

∴ 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 AND the effects of the other electron approximately.

D. Physical Picture of Integral Eq.(15) due to electron-electron interaction

Eq.(15): $$J_{1s,1s} = \iint \phi^*_{1s}(\vec{r}_1)\,\phi^*_{1s}(\vec{r}_2)\,\frac{e^2}{4\pi\varepsilon_0|\vec{r}_1-\vec{r}_2|}\,\phi_{1s}(\vec{r}_1)\,\phi_{1s}(\vec{r}_2)\,d^3r_1\,d^3r_2 \qquad (15)$$

[call it J]

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

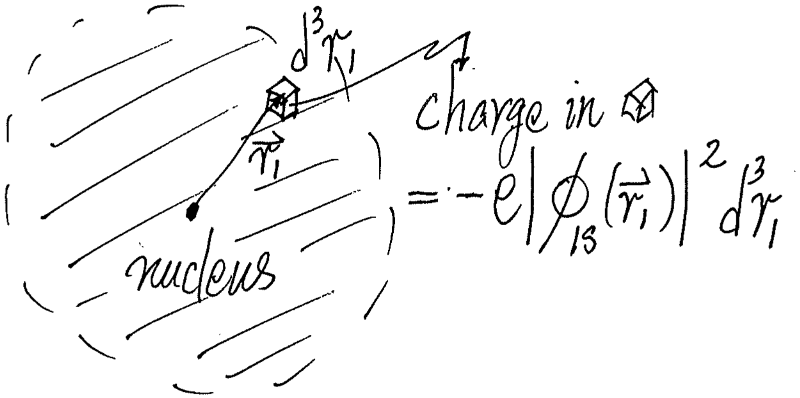
$$= \iint \underbrace{\frac{\rho_{1s}(\vec{r}_1)\,d^3r_1\cdot\rho_{1s}(\vec{r}_2)\,d^3r_2}{4\pi\varepsilon_0\,|\vec{r}_1-\vec{r}_2|}}_{\sim\ \frac{Q_1Q_2}{4\pi\varepsilon_0|\vec{r}_1-\vec{r}_2|}\ \text{\& add up all contributions}}$$

← looks very E&M like!

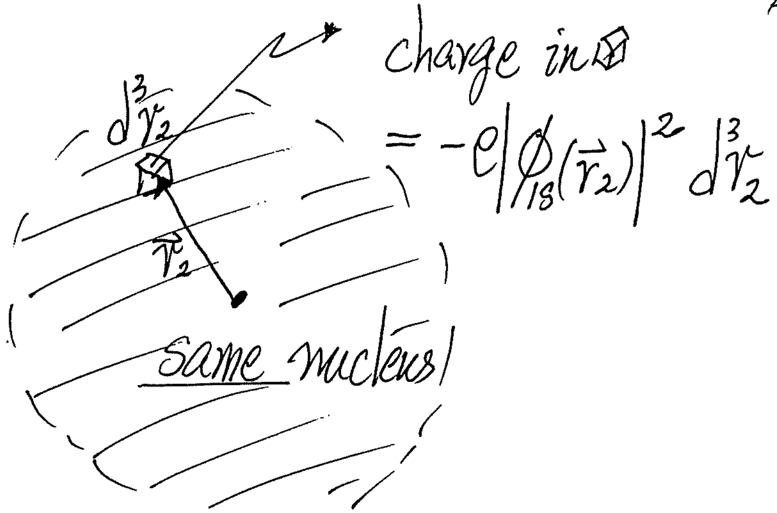
$$\underbrace{\rho_{1s}(\vec{r}_1)}_{\text{charge density at }\vec{r}_1\text{ due to electron 1}} \equiv \underbrace{-e}_{\text{charge of electron}}\ \underbrace{|\phi_{1s}(\vec{r}_1)|^2}_{\text{prob. density of finding electron 1 at }\vec{r}_1} \Rightarrow \underbrace{\rho_{1s}(\vec{r}_1)\,d^3r_1}_{\text{charge in volume element } d^3r_1 \text{ at } \vec{r}_1 \text{ due to electron 1}}$$

(if it is in a state called ϕ_{1s})

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



Electron 1 in state ϕ_{1s}



Electron 2 in state ϕ_{1s}

- Coulomb interaction between patches of charge

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

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

$$= \iint \frac{\left(-e|\phi_{1s}(\vec{r}_1)|^2\right)\left(-e|\phi_{1s}(\vec{r}_2)|^2\right) d^3r_1\, d^3r_2}{4\pi\varepsilon_0 |\vec{r}_1 - \vec{r}_2|} \quad \text{(which is Eq. (15))}$$

i.e. interaction potential energy due to Coulomb interaction

- Interpretation of Eq.(15) 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. (15) OR (23): Write as

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

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

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

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

← Mathematical form

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

an effective p.e. term due to another electron

$$= \int \phi_{1s}^{*}(\vec{r}_1)\,V_{el\text{-}el}^{(eff)}(\vec{r}_1)\,\phi_{1s}(\vec{r}_1)\,d^3r_1 \qquad (23')$$

■ 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 Hartree approximation (a powerful method in Quantum Chemistry and solid state physics)

$\therefore$ Analyzing He-atom with our tools indicates that quantum physics of an atom can be approximately treated as single-electron problems with an $V^{eff}(\vec{r})$ including (some of) the effects of the other $(Z-1)$ electrons