What about spin? Multi-electron wavefunction

$$\Psi(\vec{r}_1, s_1; \vec{r}_2, s_2; \ldots) = -\Psi(\vec{r}_2, s_2; \vec{r}_1, s_1; \ldots)$$

antisymmetric when both spin & position swapped.

Light atoms ⇒ small spin-orbit coupling

~~⇒~~ $\vec{L}\cdot\vec{S}$ due to relativity, large Z

No other terms coupling spin to $\vec{r}$

~~⇒ Independent~~

Uncoupled spin, $\vec{r}$ ⇒ Separation of Variables

– for distinguishable energy eigenstates)

$$\underbrace{\Psi^{DIST}(\vec{r}_1, s_1; \ldots)} = \psi(\vec{r}_1, \vec{r}_2, \ldots)\,\chi(s_1, s_2, \ldots)$$

Antisymmetrize → No longer factors (Li exercise) in general

⇒ Young Tableaux...

Example: He, two electrons ⇒ Eigenstates do factor

He energy eigenstates $\Psi(\vec{r}_1, s_1; \vec{r}_2, s_2) = \psi(\vec{r}_1, \vec{r}_2)\,\chi(s_1, s_2)$

Guess: Spins in ground state parallel or antiparallel?

χ ~~spin state~~ of ground state? Singlet $\chi = \frac{1}{\sqrt{2}}(\uparrow\downarrow - \downarrow\uparrow)$

Ground state $\underbrace{\psi(\vec{r}_1, \vec{r}_2)}_{\text{Symmetric, 6 dim}}(\uparrow\downarrow - \downarrow\uparrow)/\sqrt{2}$, $E = -78.95\,eV$

Why such a strong binding?

First electron $Z^2(13.6\,eV) = 54.4\,eV$

Ballpark { Ignore Coulomb repulsion, $2^{nd} \times 2 = 109\,eV$

{ 2^{nd} electron as if screened → H $\quad 54.4 + 13.6 = 61\,eV$

Triplet excited state

$$\Psi^* = \underbrace{\psi^*(\vec{r}_1, \vec{r}_2)}_{\text{Antisymmetric, 6 dim}} \chi^*(s_1, s_2) \qquad \chi^* = \underbrace{\begin{cases} \uparrow\uparrow \\ (\uparrow\downarrow + \downarrow\uparrow)/\sqrt{2} \\ \downarrow\downarrow \end{cases}}_{\text{Symmetric}}$$

$-59.13\,eV$, nodes in 6 dim WF raise energy.

Q: Is this actually an eigenstate?

A: No, eventually decays by emitting photon(s).

[Doubly forbidden: $L=0$ → no electric dipole, $S_{tot}=1$ → spin flip. → 7870 sec lifetime!)

Atomic excited states are <u>resonances</u>:

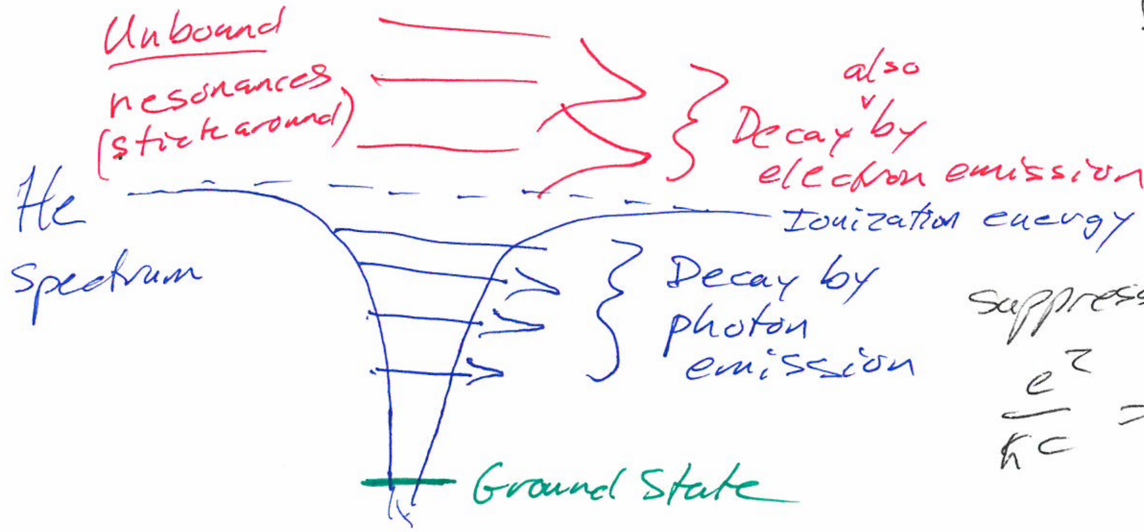
(magnetic dipole allowed relativistic, finite atom size)

- Lifetimes $10^{-15}\,s \lesssim \tau \lesssim 2$ hours
- Energies have widths

Kick atom → superposition of excited states $\Psi(\vec{r}, \vec{s}, t) \mathrel{\tilde{=}} \sum e^{-iE_n t/\hbar} \Psi_n(\vec{r}, s)$

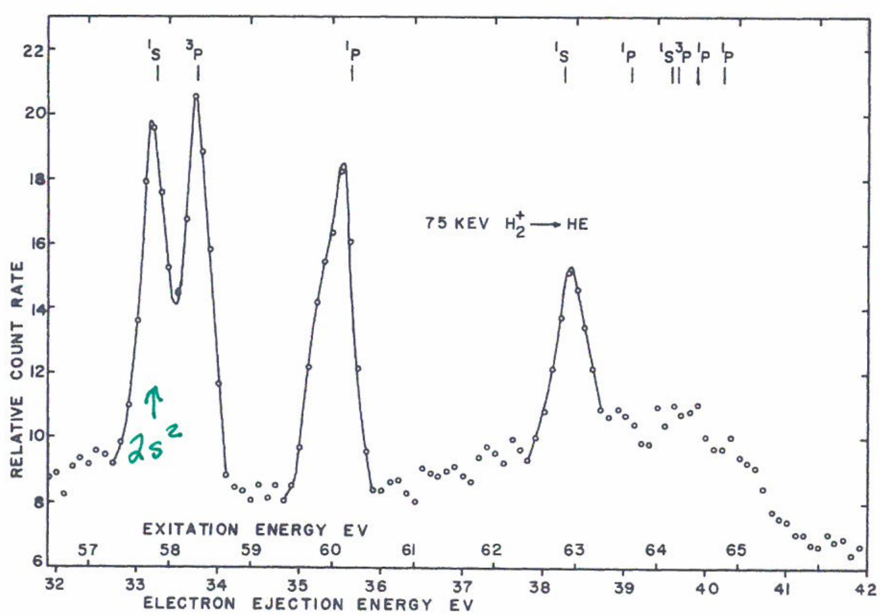
→ Excited states decay, emitting photons or electrons

→ Emitted energies $\approx (E_n - E_0) \pm \underbrace{\hbar/\tau}_{\text{Energy Uncertainty}}$



suppressed by $\frac{e^2}{\hbar c} = 1/137$

Energies of emitted electrons (Rudd, 1964)



~~Ionized~~

How do you guess where resonances will be?

Look for "unperturbed" limit where energy eigenstates are exact.

Bound resonances

→ ~~Ea~~ Unperturbed Hamiltonian ignores coupling to electromagnetism

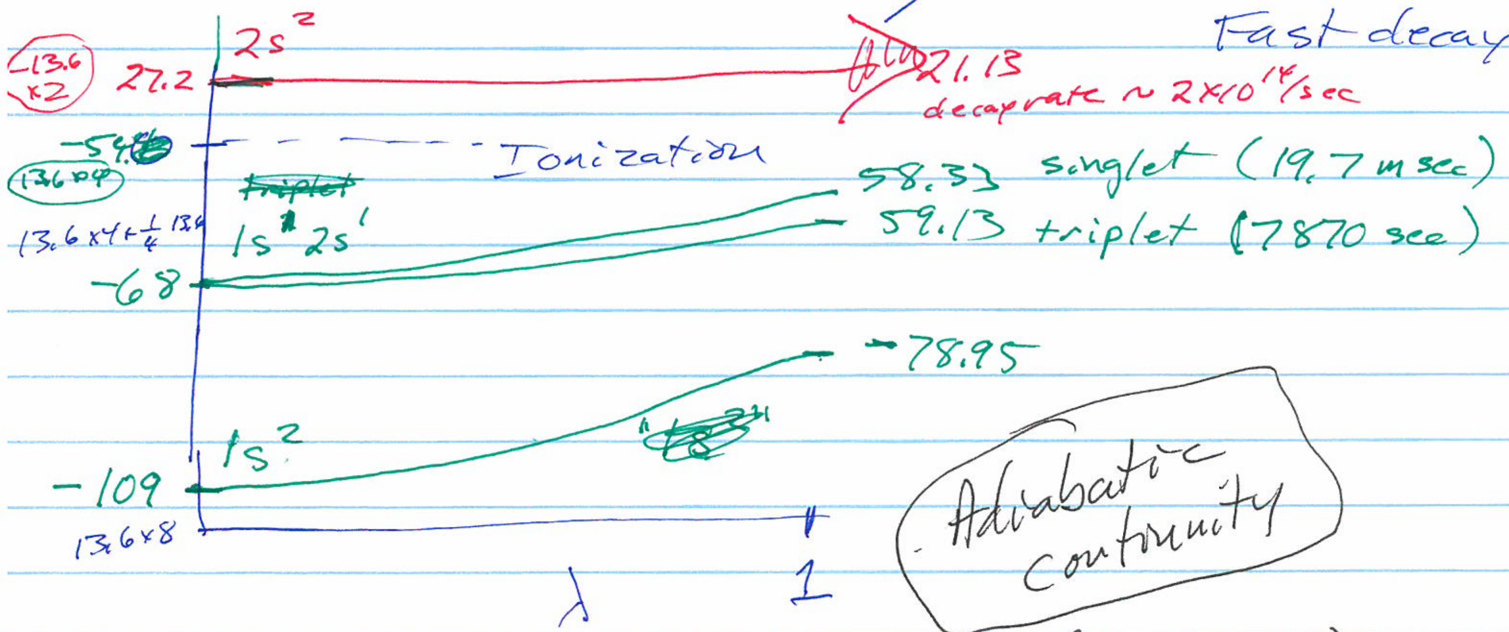
$\alpha = e^2/\hbar c$ small parameter – ignorable

Unbound resonances decay ~~due to~~ anyhow.

Unperturbed hamiltonian: Ignore e-e Coulomb repulsion!

$$\mathcal{H} = \frac{P_1^2}{2m} + \frac{P_2^2}{2m} - \frac{Ze^2}{|r_1|} - \frac{Ze^2}{|r_2|} + \frac{\lambda e^2}{|\vec{r}_1 - \vec{r}_2|}$$

Not small? 20% effect?



(resonances)

~~⊞~~ Labeling energy eigenstates by 'filled orbitals' (~~free~~ non-interacting electron states) ~~a~~ routine. Periodic Table

C
$1s^2 2s^2 2p^2$

Bogus, but useful.

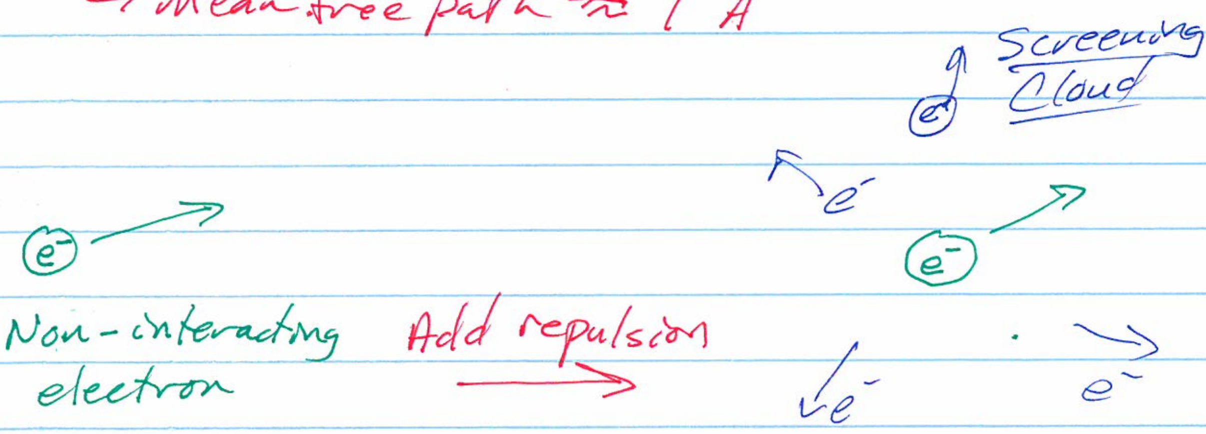
Non-interacting electron approximation
<u>also</u> useful in metals, semiconductors

'electrons' and 'holes' really <u>quasiparticles</u>.

electron ~~mobility~~ mean free path in Cu ~ 400 Å

Coulomb interaction $\frac{e^2}{|\vec{r}-\vec{r}_i|}$ of 'bare' electron with other electrons

⇒ mean free path ~ 1 Å



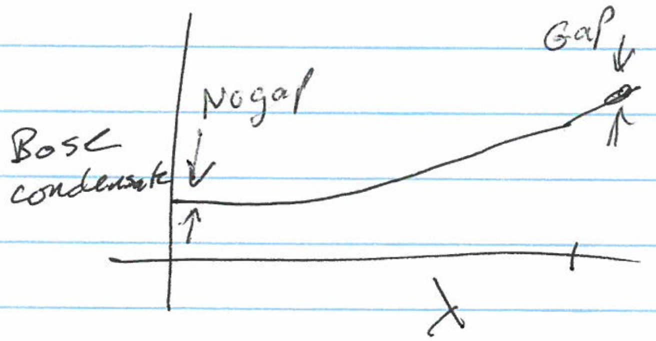
electron ~~drags around~~ 'dressed' by ~~'dressing'~~ screening cloud; <u>effective</u> lifetime much longer.

Non-interacting ~~fermions: Shortcuts~~ Bosons.

- Photons are non-interacting (almost) [Maxwell's eqns linear]
- Phonons are almost so too
- Cold Bose gas experiments weakly interacting

→ All can bose condense, macroscopic occupation of single state

He^4 atoms interact strongly.



Superfluidity is adiabatic continuation of Bose condensate.

(Explanation in terms of non-interacting bosons.)