B. Ideas in Handling multi-electron atoms

(a) Helium Atom: Ground State

- Atoms beyond H-atom are insoluble QM problems

∵ $\dfrac{e^2}{4\pi\varepsilon_0|\vec{r}_i-\vec{r}_j|}$ (electron-electron interaction) ⇒ Can't separate QM problem into single-electron problems

⇒ $\boxed{\text{Any single-electron treatment is an approximation}}$

But this is the best way out! (Can make use of knowledge from hydrogen)

Helium Problem

$$\hat{H}_{He} = \left(\frac{-\hbar^2}{2m}\nabla^2_{\vec{r}_1} - \frac{2e^2}{4\pi\varepsilon_0 r_1}\right) + \left(\frac{-\hbar^2}{2m}\nabla^2_{\vec{r}_2} - \frac{2e^2}{4\pi\varepsilon_0 r_2}\right) + \underbrace{\frac{e^2}{4\pi\varepsilon_0|\vec{r}_1-\vec{r}_2|}}_{\text{killed the problem (insoluble!)}} \qquad (7)$$

e^- #1 problem (OK! Hydrogen-like)

e^- #2 problem (OK! Hydrogen-like)

Save the Single-Electron Picture

$\overline{\uparrow\downarrow}$ some He-atom 1s state
(picture of He G.S.)

$$\Psi^{GS}_{He}(\vec{r}_1,\vec{r}_2) = \underbrace{\phi^{(He)}_{1s}(\vec{r}_1)\cdot\phi^{(He)}_{1s}(\vec{r}_2)}_{\text{Spatial Part is symmetric}}\cdot\underbrace{\frac{1}{\sqrt{2}}\left[\alpha_1\beta_2-\alpha_2\beta_1\right]}_{\text{Spin part is anti-symmetric}} \qquad (8)$$

must be anti-symmetric for 2-electron wavefunction w.r.t. interchanging

Do not know what $\phi_{1s}(\vec{r})$ is!

spin up spin wavefunction $\begin{pmatrix}1\\0\end{pmatrix}$

spin down spin wavefunction $\begin{pmatrix}0\\1\end{pmatrix}$

$\hat{S}_z = \frac{\hbar}{2}\begin{pmatrix}1&0\\0&-1\end{pmatrix}$

(This is called "Spin Singlet" state, with total spin quantum number $S=0$)

- This enforces a single-electron description (an approximation)
- Leaving $\phi^{(He)}_{1s}(\vec{r})$ yet-to-be-determined
- Find sensible way to determine $\phi^{(He)}_{1s}$

Math Picture Leading to a Physical Picture

- Even $\phi_{1s}^{(He)}(\vec{r})$ is not known yet, we could use $\psi_{He}^{GS}(\vec{r}_1,\vec{r}_2)$ to find the Ground State Expectation Value

$$\langle \psi_{He}^{GS} | \hat{H}_{He} | \psi_{He}^{GS} \rangle \equiv \int \psi_{He}^{GS*}(\vec{r}_1,\vec{r}_2)\, \hat{H}_{He}\, \psi_{He}^{GS}(\vec{r}_1,\vec{r}_2)\, d^3r_1\, d^3r_2 \cdot \overbrace{(\text{Inner product of spin part})}^{=1}$$

(∵ $\hat{H}_{He}$ has no spin-dependent term)

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

$$= I_1 + I_2 + \int \phi_{1s}^{*}(\vec{r}_1) \underbrace{\left((-e) \int \frac{(-e)\, |\phi_{1s}(\vec{r}_2)|^2}{4\pi\varepsilon_0 |\vec{r}_1 - \vec{r}_2|}\, d^3r_2 \right)}_{\text{"}\vec{r}_2\text{" is integrated over (function of } \vec{r}_1)} \phi_{1s}(\vec{r}_1)\, d^3r_1 \qquad (9)$$

I_1, I_2: actually they are equal (even don't know what ϕ_{1s} is)

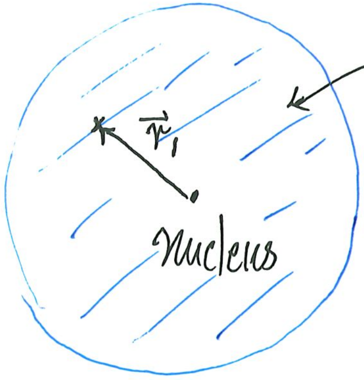
$$V^{eff}_{\text{due to electron \#2}}(\vec{r}_1)$$

Suggesting that when we focus on electron 1, electron 2 in $\phi_{1s}(\vec{r})$ is contributing an Effective Single-Electron Potential Energy Function $V^{eff}(\vec{r}_1)$ on Electron 1

$$V^{eff}(\vec{r}_1) = \frac{e^2}{4\pi\varepsilon_0}\int \frac{|\phi_{1s}(\vec{r}_2)|^2}{|\vec{r}_1-\vec{r}_2|}\, d^3r_2 \qquad (10) \quad \text{(Direct Coulomb term)}$$

Electron 1 thinks

"Electron 2 in (unknown) ϕ_{1s}, thus $|\phi_{1s}(\vec{r}_2)|^2 d^3r$ is probability of finding it at $\vec{r}_2$ in volume element d^3r, this bit of electron 2 will create an electric potential $\frac{-e|\phi_{1s}(\vec{r}_2)|^2}{4\pi\varepsilon_0|\vec{r}_1-\vec{r}_2|}$ at my position $\vec{r}_1$, and so a potential energy $\frac{e^2}{4\pi\varepsilon_0|\vec{r}_1-\vec{r}_2|}$. Total effect of electron 2 is found by adding up its effect bit by bit, so $\frac{e^2}{4\pi\varepsilon_0}\int\frac{|\phi_{1s}(\vec{r}_2)|^2}{|\vec{r}_1-\vec{r}_2|}d^3r_2$"



To Electron 1, Electron 2 is $\underbrace{\text{spread out}}_{\text{this is the approximation}}$ according to $|\phi_{1s}^{He}(\vec{r}_2)|^2$

and generates $V^{eff}(\vec{r}_1)$ on electron 1

With this physical picture, $\phi_{1s}^{He}(\vec{r})$ can be determined approximately by

$$\left[-\frac{\hbar^2}{2m}\nabla^2 - \frac{2e^2}{4\pi\varepsilon_0 r} + \underbrace{\frac{e^2}{4\pi\varepsilon_0}\int\frac{|\phi_{1s}^{He}(\vec{r}\,')|^2\,d^3r'}{|\vec{r}-\vec{r}\,'|}}_{\text{an approximated way to handle el-el interaction}}\right]\phi_{1s}^{He}(\vec{r}) = \varepsilon_{1s}^{He}\,\phi_{1s}(\vec{r}) \qquad (11)$$

to solve

But $V^{eff}(\vec{r})$ needs $|\phi_{1s}^{He}(\vec{r})|^2$ as input, before we have an equation to solve for $\phi_{1s}^{He}(\vec{r})$!

Self-consistent Approach: Guess $\phi_{1s}^{He}(\vec{r}) \to V^{eff} \to$ solve for $\phi_{1s}^{He}(\vec{r}) \to$ Compare input with output $\to$ adjust $\phi_{1s}^{He}(\vec{r}) \to V^{eff} \to \cdots$ (until convergence)

Key Physical Idea

$$V_{\text{bare}}(r) = \frac{-2e^2}{4\pi\varepsilon_0 r} \qquad \text{(one electron sees nucleus of +2e charge)}$$

But when we treated the other electron(s) in an atom in an averaged way, there will be additional term(s). Here we see the Direct Coulomb Term.

$$\therefore \left[-\frac{\hbar^2}{2m}\nabla^2 \underbrace{- \frac{2e^2}{4\pi\varepsilon_0 r} + V^{\text{eff}}(\vec{r})}_{\text{altogether NOT of Coulomb form } (-\frac{1}{r} \text{ form})} \right] \phi_{1s}^{He}(\vec{r}) = \varepsilon_{1s}^{He} \phi_{1s}(\vec{r})$$

$$\Rightarrow \boxed{\text{expect } \varepsilon_{\underset{\substack{\uparrow \\ \text{depends on } n \text{ and } l}}{\underbrace{nl}}} \text{ for atoms}} \qquad (12)$$

$$\frac{e^2}{4\pi\varepsilon_0}\int\frac{|\phi_{1s}^{He}(\vec{r}')|^2 d^3r'}{|\vec{r}-\vec{r}'|}$$ is the Direct Coulomb Term

It is the Hartree Approximation.

- The same approximation can be applied to solids
- It is related to the Hartree-Fock Approximation. But there is NO "Fock" term in the He Ground state problem because the spatial part involves only ONE spatial $\phi_{1s}^{He}(\vec{r})$ centered at the (one) nucleus.
- This is a mean-field theory (self-consistent field theory).

For this method applied to Helium Ground state,

$$E^{(GS)}_{\text{Hartree}} = \underset{\text{(no Fock term)}}{E^{(GS)}_{HF}} = -77.8708 \text{ eV} \qquad \left(\underset{\text{(for Helium)}}{E^{(GS)}_{\text{actual}}} = -79.0137 \text{ eV} \right)$$

↑ best value within Hartree-Fock approximation

$$E_{\text{actual}} - E_{HF} \equiv \text{Correlation Energy} \quad \text{(definition)} \tag{13}$$

↗ exp'tal or best numerical value beyond HF

⇒ Strongly correlated electron systems are those mean-field HF approximation doesn't work so well

(b) Other atoms

- $\underbrace{\text{More electrons}}$
- Electrons need to go into more $\underbrace{\overset{\text{single-particle}}{\text{s.p.}}\text{ states}}_{\phi_a,\ \phi_b,\ \phi_c}$ (∵ Pauli Exclusion)

↑

ψ (many electrons) must be antisymmetric w.r.t. interchanging coordinates of two electrons

[Spin wavefunction]

⇒ will have $[\phi_a(\vec{r}_1)\,\phi_b(\vec{r}_2) \pm \phi_a(\vec{r}_2)\,\phi_b(\vec{r}_1)]$ (2-electron example)

∴ Will see

$$K_{a,b} \equiv \iint \phi_a^*(\vec{r}_1)\,\phi_b^*(\vec{r}_2)\,\frac{e^2}{4\pi\varepsilon_0|\vec{r}_1-\vec{r}_2|}\,\phi_a(\vec{r}_2)\,\phi_b(\vec{r}_1)\,d^3r_1\,d^3r_2 \qquad (14)$$

in addition to [exchange Coulomb integral, NO Classical interpretation]

$$J_{a,b} \equiv \iint \phi_a^*(\vec{r}_1)\,\phi_b^*(\vec{r}_2)\,\frac{e^2}{4\pi\varepsilon_0|\vec{r}_1-\vec{r}_2|}\,\phi_a(\vec{r}_1)\,\phi_b(\vec{r}_2)\,d^3r_1\,d^3r_2 = \int \phi_a^*(\vec{r}_1)\int\frac{e^2|\phi_b(\vec{r}_2)|^2\,d^3r_2}{4\pi\varepsilon_0|\vec{r}_1-\vec{r}_2|}\,\phi_a(\vec{r}_1)\,d^3r_1 \qquad (15)$$

[Direct Coulomb integral]

Exchange Term

$$K_{a,b} \equiv \iint \phi_{a}^{*}(\vec{r}_1)\, \phi_b^{*}(\vec{r}_2)\, \frac{e^2}{4\pi\varepsilon_0 |\vec{r}_1 - \vec{r}_2|}\, \phi_a(\vec{r}_2)\, \phi_{b}(\vec{r}_1)\, d^3r_1\, d^3r_2 \qquad (14)$$

different single-part states

which is DIFFERENT from

$$J_{a,b} \equiv \iint \phi_a^{*}(\vec{r}_1)\, \phi_b^{*}(\vec{r}_2)\, \frac{e^2}{4\pi\varepsilon_0 |\vec{r}_1 - \vec{r}_2|}\, \phi_a(\vec{r}_1)\, \phi_b(\vec{r}_2)\, d^3r_1\, d^3r_2$$

→ this gives a Coulomb operator on $\phi_a(\vec{r}_1)$ as

$$\hat{J}_b(\vec{r}_1)\, \phi_a(\vec{r}_1) = \phi_a(\vec{r}_1) \underbrace{\left[\int \phi_b^{*}(\vec{r}_2)\, \frac{e^2}{4\pi\varepsilon_0 |\vec{r}_1 - \vec{r}_2|}\, \phi_b(\vec{r}_2)\, d^3r_2 \right]}_{\text{an operator (Hartree term)}}$$

But the Exchange Term gives an exchange operator on $\phi_a(\vec{r}_1)$ as

$$\hat{K}_b(\vec{r}_1)\,\phi_a(\vec{r}_1) = \phi_a(\vec{r}_1)\underbrace{\int \phi_b^*(\vec{r}_2)\,\frac{e^2}{4\pi\varepsilon_0|\vec{r}_1-\vec{r}_2|}\,\phi_a(\vec{r}_2)\,d^3r_2}_{\substack{\text{different states}\\ \text{operator (depends on }\vec{r}_1)}}$$

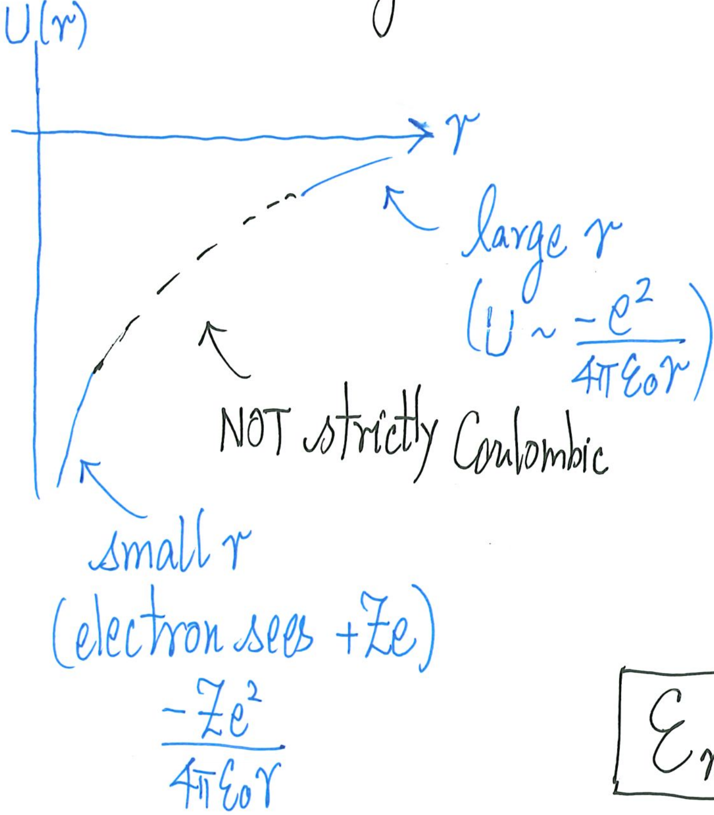
which will appear in equation for determining $\phi_a(\vec{r}_1)$ [and $\phi_b(\vec{r}_1)$]

Take-Home message

There will be Direct Coulomb and Exchange Coulomb terms in the Schrödinger-like single-electron equations when reducing a many-electron atomic problem to single-electron problems.

+ Generally, we should consider Li, Be, B, C, ··· Ground states to introduce the exchange term. What we did here is the easiest/simplest situation in which the exchange term appears.

∴ What the single electron sees effectively is quite complicated!



("screened" by other electrons)

effects of Direct and Exchange Terms
(Hartree-Fock Approximation)

$\boxed{\varepsilon_{nl}}$ $\qquad \varepsilon_{3s} \neq \varepsilon_{3p}$

It is with this complicated HF treatment that an atom gets its atomic orbitals (1s, 2s, 2p, 3s, 3p, ...), from which they can form bonds!

Classic Reference: Blinder, "Basic Concepts of Self-Consistent-Field Theory", Am. J. Phys. 33, 431 (1965), discussses HF as a variational calculation.

(c) Further appreciation of the Band Problem in Solids

- Atomic $U(r)$ is non-trivial to determine
- What to try for the $\underbrace{\text{periodic } U(\vec{r})}$ in a solid?
  - electron see array of nuclei
  - $\underbrace{\text{all other electrons}}$ [Hartree-Fock effects]
  - will contribute to $\underbrace{U(\vec{r})}$

determines $\underbrace{\psi_{n\vec{k}}(\vec{r})}$

occupied states $\Rightarrow$ $\underbrace{n(\vec{r})}$

electron charge density

$\Downarrow$

$U(\vec{r})$ again

$\Downarrow$

$\vdots$ (self-consistency)

- Keep "Core electrons" to nucleus and consider ions?

$\left[\frac{-\hbar^2}{2m}\nabla^2 + U(\vec{r})\right]\psi_{\vec{k}}(\vec{r}) = E(\vec{k})\,\psi_{\vec{k}}(\vec{r})$ is non-trivial to set up!

(d) Taking Hartree-Fock (Direct/Exchange) into Energy Band Problem

Reducing many-electron problem to single-electron problems (look for Bloch states)

$$\hat{H} = \frac{-\hbar^2}{2m}\nabla^2 + V_{el\text{-}ions} + \left(\begin{array}{c}\text{approximation on el-el interaction}\\ \text{in mean field way}\end{array}\right)$$

Roughly (just a sense on the complexity of the problem)

$$\left\{\frac{-\hbar^2}{2m}\nabla^2 + V_{el\text{-}ions} + \frac{e^2}{4\pi\varepsilon_0}\sum_{\substack{j\\(\text{occupied})}}\int d^3r' \frac{|\phi_j(\vec{r}')|^2}{|\vec{r}-\vec{r}'|}\right\}\boxed{\phi_i(\vec{r})}$$

$$-\frac{e^2}{4\pi\varepsilon_0}\sum_{\substack{j\\(\text{occupied})}}\int d^3r' \frac{\phi_j^*(\vec{r}')\boxed{\phi_i(\vec{r}')}}{|\vec{r}-\vec{r}'|}\phi_j(\vec{r}) = \boxed{\varepsilon_i}\boxed{\phi_i(\vec{r})}$$

and similar equations for $\phi_j(\vec{r})$'s [set of equations]

(self-consistent)

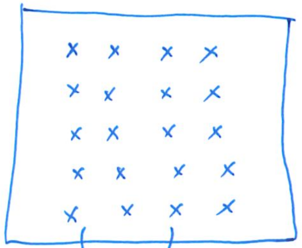
[See Balkanski and Wallis, Ch.3]

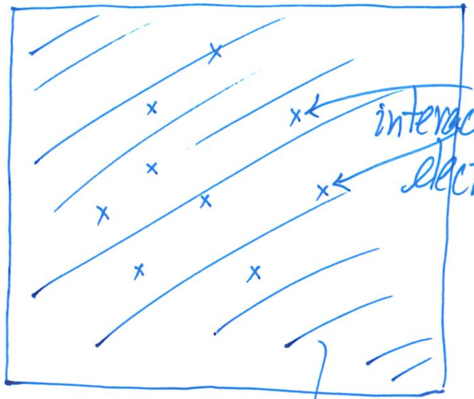
Aside: Beginning of Many-Body Theory

- Electron Gas problem
  - Positive charged uniform background [not isolated ions] plus interacting electrons
  - Hartree-Fock approximation can be carried out analytically
  - HF has corresponding Feynman diagrams

Many interesting phenomena

- screening, plasma oscillation
- dilute limit → Wigner crystal


electrons form an array



uniform +ve background

(e) Helium Atom: First excited state and Origin of Magnetism

- Picture: one electron in ϕ_{1s}, another in ϕ_{2s}

could be

2s	↑	↓	↓	↑
1s	↑	↓	↑	↓

	Spatial Part		Spin Part
$\boxed{\text{one state}}$ (S=0)	$\frac{1}{\sqrt{2}}\left[\phi_{1s}(\vec{r}_1)\phi_{2s}(\vec{r}_2)+\phi_{1s}(\vec{r}_2)\phi_{2s}(\vec{r}_1)\right]$ (symmetric)	$\cdot$	$\frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2)-\alpha(2)\beta(1)\right]$ (anti-symmetric) [singlet]
$\boxed{\text{three states}}$ (S=1)	$\frac{1}{\sqrt{2}}\left[\phi_{1s}(\vec{r}_1)\phi_{2s}(\vec{r}_2)-\phi_{1s}(\vec{r}_2)\phi_{2s}(\vec{r}_1)\right]$ (anti-symmetric)	$\cdot$	$\left\{\begin{array}{l}\alpha(1)\alpha(2)\\ \frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2)+\alpha(2)\beta(1)\right]\\ \beta(1)\beta(2)\end{array}\right.$ (symmetric) [triplet]

Q: Will $S=0$ state and $S=1$ states have different energies?

$$\hat{H}_{He} = \hat{h}_1 + \hat{h}_2 + \frac{e^2}{4\pi\varepsilon_0 |\vec{r}_1 - \vec{r}_2|}$$

[<u>Note</u>: $\hat{H}_{He}$ has no terms depending on spins. But value of S turns out to be important!]

<u>$S=0$ state</u> (singlet)

$$E_{singlet} = \iint \frac{1}{2}\left[\phi_{1s}^*(\vec{r}_1)\phi_{2s}^*(\vec{r}_2) + \phi_{1s}^*(\vec{r}_2)\phi_{2s}^*(\vec{r}_1)\right] \hat{H}_{He} \left[\phi_{1s}(\vec{r}_1)\phi_{2s}(\vec{r}_2) + \phi_{1s}(\vec{r}_2)\phi_{2s}(\vec{r}_1)\right] d^3r_1\, d^3r_2$$

<u>$S=1$ state</u> (triplet)

$$E_{triplet} = \iint \frac{1}{2}\left[\phi_{1s}^*(\vec{r}_1)\phi_{2s}^*(\vec{r}_2) - \phi_{1s}^*(\vec{r}_2)\phi_{2s}^*(\vec{r}_1)\right] \hat{H}_{He} \left[\phi_{1s}(\vec{r}_1)\phi_{2s}(\vec{r}_2) - \phi_{1s}(\vec{r}_2)\phi_{2s}(\vec{r}_1)\right] d^3r_1\, d^3r_2$$

[They are <u>not the same</u>, by inspection]

Roughly,

$$E_{singlet} = \underbrace{[\text{some terms}]}_{I \,\&\, J_{1s,2s}} + \text{terms like} \iint \phi^*_{1s}(\vec{r}_1)\,\phi^*_{2s}(\vec{r}_2)\,\frac{e^2}{4\pi\varepsilon_0|\vec{r}_1-\vec{r}_2|}\,\phi_{1s}(\vec{r}_2)\,\phi_{2s}(\vec{r}_1)\,d^3r_1\,d^3r_2$$

(Direct term)

called $K_{1s,2s}$ (Exchange term)

$$E_{triplet} = \overbrace{[\text{some terms}]} - \text{terms like} \overbrace{\iint \phi^*_{1s}(\vec{r}_1)\,\phi^*_{2s}(\vec{r}_2)\,\frac{e^2}{4\pi\varepsilon_0|\vec{r}_1-\vec{r}_2|}\,\phi_{1s}(\vec{r}_2)\,\phi_{2s}(\vec{r}_1)\,d^3r_1\,d^3r_2}$$

- $K_{1s,2s}$ has no classical analogy [inspect states and coordinates] (entirely quantum)
- called exchange Coulomb integral (or indirect Coulomb integral)

∴ $E_{triplet} \neq E_{singlet}$ due to $K_{1s,2s}$ term (which can be negative or positive)

In Helium atom, $E_{triplet} < E_{singlet}$ ⇒ Triplet Spin state is energetically preferred

Triplet $\underbrace{(S=1)}_{\text{two spins tend to align}}$ versus Singlet $\underbrace{(S=0)}_{\text{two spins tend to antialign}}$

determined by the sign of the $\underbrace{\underline{\text{Exchange Coulomb integral}}}_{\substack{\text{this is the Heisenberg exchange interaction}\\ \text{mechanism of Ferromagnetism}}}$

$$-\underset{\substack{\nearrow\\ \text{exchange}\\ \text{energy}\\ (K>0)}}{K}\;\underbrace{\underset{\substack{\uparrow\\ +1\\ \text{OR}\\ -1}}{\vec{\sigma}_i}\cdot\underset{\substack{\uparrow\\ +1\\ \text{OR}\\ -1}}{\vec{\sigma}_j}}_{\text{prefers alignment}}$$