At the time of the Stern-Gerlach Expt, the order of filling $\text{e}^-$ into orbitals was approximately determined, but not quite worked out. We now know $A_g^\text{e}^- = 4d^{10}5s^1$ configuration.

They were trying to measure distribution of orbital angular momentum magnetic field states.

They expected that B-field exerts force on magnetic dipole moment of each atom, deflecting it up/down according to the orientation of $m$ (magnetic dipole moment).

We know that each $l$ is split into $2l+1$ $m$-values of projection onto a fixed axis, so it's expected to get 1, 3, 5, etc. Bands of atoms split by deflection of B-field.

* They observed $A_g^\text{e}^-$ atoms hitting phosphor screen split into 2 bands! Unexpected...

* With orbital angular momentum, no way to get 2

It took a few years to explain this observation. Turns out that an intrinsic angular momentum of $\text{e}^-$ "spin" is responsible for this splitting.

$e^-$ angular momentum $s = \frac{1}{2}$ ($l$ is not used)

So $m_s = 2s+1 = 2$ orientations: $\pm \frac{1}{2}$ up & down

Relativistic Q.M. (Dirac Eq.) predicts that all elementary particles have an intrinsic "spin"
CHEM 4531 FALL 2015  \( \epsilon \) - SPIN

We will encounter two categories of particles:

- Fermions (\( S = \frac{1}{2} \)) \( \epsilon \), protons, some nuclei
- Bosons (\( S = 1 \)) photons, some nuclei

For \( \epsilon \), \( M_s = \frac{1}{2}, -\frac{1}{2} \) are the spin quantum numbers. 
\( S_z = \frac{1}{2} \hbar, -\frac{1}{2} \hbar \) are the z-component of spin.
\( S = \frac{\hbar}{\sqrt{2S(S+1)}} = \frac{\hbar \sqrt{3}}{2} \hbar \) is the spin eigenvalue.

Spin is just like any other angular momentum!

So what is the spin eigenfunction? It has no spatial coordinate dependence.

\( \alpha = \text{spin up} \quad |\alpha\rangle \)
\( \beta = \text{spin down} \quad |\beta\rangle \)

They are orthonormal so
\( \langle \alpha | \alpha \rangle = \langle \beta | \beta \rangle = 1 \)
\( \langle \alpha | \beta \rangle = \langle \beta | \alpha \rangle = 0 \)

The Dirac equation leads to a new postulate of quantum mechanics:

The wavefunction for any system of electrons (fermions) must be antisymmetric with respect to exchange of any two electrons (Pauli Principle).

E.g. given an atomic wavefunction for two \( \epsilon \):
\[ \psi(1, 2) \]
Then swapping \( 1 \to 2 \) changes sign.

So \[ \psi(1, 2) = -\psi(2, 1) \]

But \[ |\psi(2, 1)|^2 = |\psi(1, 2)|^2 \]

\( \rightarrow \) Probability density doesn't change.
CONSEQUENCE OF PAULI PRINCIPLE FOR ELECTRONIC STRUCTURE...

Consider a two electron atom with non-interacting e⁻ and simplified Hamiltonian $\hat{H} = \hat{H}_1 + \hat{H}_2$.

$\Rightarrow \hat{H}_1 \psi_1 = E_1 \psi_1 \quad \hat{H}_2 \psi_2 = E_2 \psi_2$ for each e⁻ (separable). Consider the possibility that both e⁻ are in the same orbital $\psi_1 = \psi_2 = \psi_A$. The overall wavefunction will be $\psi_A(1) \psi_A(2)$. If we include the various possibilities for spin states of the two e⁻, we can write:

1. $\psi_A(1) \psi_A(2) \alpha(1) \alpha(2)$ both up spin
2. $\psi_A(1) \psi_A(2) \beta(1) \beta(2)$ both down
3. $\psi_A(1) \psi_A(2) [\alpha(1) \beta(2) + \alpha(2) \beta(1)]$ linear combinations of up/down
4. $\psi_A(1) \psi_A(2) [\alpha(1) \beta(2) - \alpha(2) \beta(1)]$

Test #1 $\Rightarrow$ #4 for consistency with Pauli Principle: 1-3 all have same sign when labels 1, 2 are swapped

But #4 is different. In this case,

$[\alpha(1) \beta(2) - \alpha(2) \beta(1)] \rightarrow [\alpha(2) \beta(1) - \alpha(1) \beta(2)]$

So $\psi(1,2) = -\psi(2,1)$

The wavefunction is anti-symmetric with respect to exchange of electrons.

This result means that if two e⁻ have same values of $\tilde{z}$, $\tilde{L}$, $\tilde{M}$, then their spins ($\tilde{M}_S$) must be "paired" - one is "up" $\frac{1}{2}$, one "down" $-\frac{1}{2}$. 
PAULI EXCLUSION PRINCIPLE - NO TWO \( e^- \) IN AN ATOM CAN HAVE THE SAME SET OF QUANTUM NUMBERS - \( 2e^-, \text{orbitals} \)

IF THE TWO (OR MORE) \( e^- \) ARE IN DIFFERENT ORBITALS, THE PAULI PRINCIPLE STILL APPLIES - TOTAL ANTISYMMETRY NECESSARY!

IN THIS CASE IT'S NECESSARY TO LOOK AT SPATIAL ORBITAL AND SPIN PARTS OF THE TOTAL SPIN ORBITAL WAVEFUNCTIONS SEPARATELY.

E.G. FOR A \( 1e^- \) STATE WITH \( 1e^- \) IN \( \psi_a \), ONE IN \( \psi_b \)

THE SPATIAL PART IS A LINEAR COMBINATION

\[
\phi_s = \psi_a(1) \psi_b(2) + \psi_a(2) \psi_b(1)
\]

\( e^- \) ARE INDISTINGUISHABLE - SO THE LINEAR COMBINATION IS NECESSARY. HOWEVER, \( \phi_+ \) EACH HAVE THEIR OWN SYMMETRY: \( \phi_+ \) SYMMETRIC, \( \phi_- \) IS ANTI-SYMMETRIC

THE SPIN PARTS NEED TO PRESERVE OVERALL ANTISYMMETRY

SO \( \phi_+ \) NEEDS AN ANTI SYMMETRIC SPIN WAVEFUNCTION

\( \phi_- \) NEEDS A SYMMETRIC SPIN WAVEFUNCTION

\[
\rightarrow \phi_+ \left[ \alpha(1) \beta(2) - \alpha(2) \beta(1) \right]
\]

PRODUCTS

\[
\rightarrow \phi_- \left[ \alpha(1) \alpha(2) \right], \phi_- \left[ \beta(1) \beta(2) \right]
\]

\( \phi_- \) SYMMETRIC

\[
\phi_- \left[ \alpha(1) \beta(2) + \alpha(2) \beta(1) \right]
\]

NOTE THAT \( \phi_+ \) HAS A SINGLE SPIN STATE (SINGLET)

\( \phi_- \) HAS THREE SPIN STATES (TRIPLET)

\( \phi_+ \) SPINS \( \frac{1}{2}(\frac{1}{2} - \frac{1}{2}) = 0 \) \( \sum \text{OF SPIN QUANTUM NUMBERS} \)

\( \phi_- \) SPINS ADD TO 1
Chem 4531 Fall 2015 Spin States

The \( \alpha(1) \times \alpha(2) \) \( \beta(1) \times \beta(2) \) \( \alpha(1) \beta(2) + \alpha(2) \beta(1) \)

States are called a triplet because the total spin adds up to 1, and in the absence of a magnetic field, they are degenerate.

In presence of a field, \( S = 1 \rightarrow 2S+1 = 3 \) \( S_z \)
Spin components \( S_z = \frac{-1}{2}, 0, \frac{1}{2} \) projected onto fixed axis \( \rightarrow \) energies split.

The \( \alpha(1) \beta(2) - \beta(1) \alpha(2) \) state has total spin = 0
So \( S_z = 0 \) (nondegenerate) so that's why it's called a "Singlet" state.

In the absence of E/M fields, the energies of atomic states are set by the spatial part of the orbital wavefunction - so, how can these wavefunctions, energies be calculated?

Atoms with \( > 1 \) e\(^-\) can't be exactly solved with Q.M. - approximation methods must be used. Here's why - consider H for He atom:

\[
\hat{H} = \hat{T}_1 + \hat{T}_2 - \frac{1}{4\pi\epsilon_0} \left( \frac{2e^2}{\frac{r_1}{r_1}} + \frac{2e^2}{\frac{r_2}{r_2}} - \frac{e^2}{\frac{r_{12}}{1_{12}}} \right)
\]

\( \hat{T}_1, \hat{T}_2 \) are e\(^-\) kinetic energies
\( r_1, r_2 \) are distances of e\(^-\) #1 #2 from Z = 2 nuclei
\(-\frac{e^2}{\frac{r_{12}}{1_{12}}} \) is e\(^-\)/e\(^-\) repulsion term.

This \( \hat{H} \) is not separable!
THERE ARE TWO APPROACHES TO APPROXIMATING FOR
Q.M. PROBLEMS. 1. PERTURBATION THEORY
2. VARIATIONAL THEORY.

PERTURBATION THEORY -

COMES IN DIFFERENT VARIETIES

/ TIME-DEPENDENT \ TIME-INDEPENDENT /

1ST 2ND 3RD... 1ST 2ND 3RD...

\ NTH-ORDER \ NTH-ORDER

DEGENERATE NON-DEGENERATE

THE BASIC IDEA IS TO BREAK DOWN THE PROBLEM
INTO AN EXACTLY SOLVABLE \( \hat{H} \) WITH A CORRECTION
(I.E. PERTURBATION) TERM (5)

LET'S SAY WE CAN WRITE \( \hat{H} = \hat{H}_0 + \hat{H}' \)
WHERE THE "ZERO-ORDER HAMILTONIAN" \( \hat{H}_0 \)
\( \hat{H}_0 \phi_0 = E_0 \phi_0 \)

IS EXACTLY SOLVABLE

\( \phi_0 \) INDICATES UNPERTURBED

SOLUTIONS

\( \hat{H}' \) IS THE PERTURBATION

\( (\hat{H}_0 + \hat{H}') \psi = E \psi \)

\( E_n = E_n^{(0)} + E_n^{(1)} + E_n^{(2)} + ... \)

\( \psi_n = \phi_n^{(0)} + \phi_n^{(1)} + \phi_n^{(2)} + ... \)

THE SUBSCRIPTS ON \( \phi_n \) AND \( E_n \) INDICATE
THE ORDER OF THE CORRECTION.

WE'LL ONLY CONSIDER FIRST-ORDER PERTURBATION THEORY -

SO \( E_n = E_n^{(0)} + E_n^{(1)} \)

\( \psi_n = \phi_n^{(0)} + \phi_n^{(1)} \)
Perturbation Theory

For first-order perturbation, the correction is

\[ E_n^{(1)} = \langle \phi_n^{(0)} | \hat{H}' | \phi_n^{(0)} \rangle \]

Expectation value of perturbation energy for unperturbed wavefunction.

There is also an expression for \( E_n \):

\[ \phi_n^{(0)} = \sum_{\text{pert}} \frac{\langle \phi_m^{(0)} | \hat{H}' | \phi_n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}} \phi_m^{(0)} \]

Example: Particle in a 1-D box with a dip in the middle:

\[ V(x) \]

\[ H_0 = 0 \quad 0 < x < L \]

\[ H_0 = \infty \quad x < 0 \quad x > L \]

\[ H' = -3 \sin \left( \frac{\pi x}{L} \right) \]

\[ N = -3 \sin \left( \frac{\pi x}{L} \right) \]

What is the ground state energy?

We know \( E_1^{(0)} = \frac{\hbar^2}{8mL^2} \) for unperturbed system.

\[ E_1^{(1)} = \int_0^L \sqrt{\frac{\hbar^2}{2mL^2}} \left( -3 \sin \left( \frac{\pi x}{L} \right) \right) \sqrt{\frac{\hbar^2}{2mL^2}} \sin \left( \frac{\pi x}{L} \right) \, dx \]

\[ = -\frac{2 \hbar^2}{L} \int_0^L \sin^3 \left( \frac{\pi x}{L} \right) \, dx = -\frac{8 \hbar^2}{3\pi} \]

So \( E_1 = \frac{\hbar^2}{8mL^2} - \frac{8 \hbar^2}{3\pi} \) makes sense that \( E_1 < E_1^{(0)} \).

The first-order perturbed wavefunction \( \phi_1^{(0)} \) is basically an expansion in terms of the \( n > 1 \) eigenstates of the unperturbed particle in a box.

We won't consider the wavefunctions in this course.
CHEM 453/ FALL 2015  HE-ATOM PERTURBATION TREATMENT

LET'S GO BACK TO THE HE ATOM. (Z=2)

\[
\hat{H} = -\frac{Z^2}{2\epsilon_0} r_{e1}^2 - \frac{Z^2}{2\epsilon_0} r_{e2}^2 - \frac{Z e^2}{4\pi\epsilon_0 r_{e1}} - \frac{Z e^2}{4\pi\epsilon_0 r_{e2}}
\]  

\[
+ \frac{e^2}{4\pi\epsilon_0 1/2^2}
\]

\[\text{e}^{-r_{e1} e_{1/2}} \text{repulsion}\]

\[\hat{H} = \hat{H}_0 + \hat{H}' \text{ where } \hat{H}' \text{ is the } e/e' \text{ term} \]

IF WE SET \(\hat{H}' = 0\) \(\rightarrow\) TOTAL WAVEFUNCTION OF THE HE ATOM GROUND STATE IS DESCRIBED BY A SEPARABLE HAMILTONIAN - ENERGY IS A SUM OF GROUND-STATE (\(n=1\)) ENERGIES \(E_1^0 = Z^2 e\)

WHERE \(E_1 = -\frac{Z^2}{2}(15.605\text{eV})/\alpha^2 \text{ with } n_1 = 1, Z = 2\)

SO \(E_1^{(0)} = -BRH = -108.8\text{ eV}\)

PERTURBATION CORRECTION: \(E_1^{(1)} = \langle \psi^{(0)} | \hat{H}' | \psi^{(0)} \rangle\)

RECALL THAT \(\psi(r, \theta, \phi) = R(r) \times Y_2^m(\theta, \phi)\)

AND \(\hat{H}' = \frac{e^2}{4\pi\epsilon_0 1/2^2}\) SO NO NEED TO CONSIDER \(Y_2^m\)

\[R_1(r) = \frac{2r^{3/2}}{a_0^{3/2}} e^{-2r/a_0} \; \text{similar for } R_2(r)\]

\[E_1^{(1)} = (4\pi^3/\alpha_0^3) \int_0^{a_0} e^{-2r/a_0} e^{-2\sqrt{2}a_0} e^{2} (1 - \frac{r}{a_0}) r_1 r_2 \text{ d}r_1 \text{ d}r_2\]

(REMEMBER THAT GROUND STATE RADIAL WAVEFUNCTION (ZERO-ORDER) IS A PRODUCT OF THE TWO IS \(R(r)\) FUNCTIONS)

AFTER LOTS OF ALGEBRA...
CHEM 4531  FALL 2015  PERTURBATION THEORY (He)

Result is \( E_1^{(1)} = \frac{57}{4}, R_1 = \frac{5}{2} (13.606 \text{ eV}) \)

\[ = 34 \text{ eV} \]

So \( E_1 = E_1^{(0)} + E_1^{(1)} \)

\[ = -108.8 \text{ eV} + 34 \text{ eV} = -74.8 \text{ eV} \]

Experimental value is \(-79.0 \text{ eV}\).

So first-order correction helps a lot! \((5\% \text{ error})\)

Q?

How to measure? 2 separate ionization events \(\Rightarrow\) sum to \(-79.1 \text{ eV}\).

For the perturbed wavefunction, the effect of the first-order correction is to add contributions from configurations other than \(1s_1^1 1s_5^5 \) (or \( 1s^2 \)) - this effect is called "configuration interaction". Quantum chemists spend a lot of time considering this effect.

Now that we have a taste of perturbation theory, let's look at the other approach for approximate solutions to Q.M. problems - the variational method.

\[ \text{If a trial wavefunction} \psi \text{ is used to calculate the ground-state energy of a quantum system, the value obtained is never less than the true energy:} \]

\[ \langle \psi | \hat{H} | \psi \rangle \geq E_1 \]

\( \langle \psi | \psi \rangle \)

or

\[ \langle \psi | \hat{H} | \psi \rangle \geq E_1 \]

\( \text{if} \ \psi \text{ is normalized} \)
VARIATION METHOD IS USEFUL FOR FINDING THE GROUND-STATE WAVEFUNCTION BECAUSE ONE CAN USE A TRIAL FUNCTION \( \Psi' \) WITH SOME ADJUSTABLE PARAMETERS, AND VARY THEIR VALUES TO MINIMIZE THE EXPECTATION VALUE ...

EXAMPLE VARIATIONAL PROBLEM?

QUANTUM CHEMISTRY

A TYPE OF COMPUTATIONAL CHEMISTRY IN WHICH ORBITAL ENERGIES ARE CALCULATED WITH APPROXIMATION METHODS FOR SOLVING THE MULTI-ELECTRON SCHRODINGER EQUATION FOR ATOMS (MOLECULES).

THERE ARE MANY METHODS, BOTH AB-INITIO (FIRST PRINCIPLES) AND SEMI-EMPirical (SOME PARAMETERS ADJUSTED TO MATCH EXPERIMENTS)

HARTREE-FOCK /SELF-CONSISTENT FIELD METHOD (HF/SCF)

* FIRST APPROXIMATION - ASSUME THAT MULTI-\( e^- \) WAVEFUNCTION CAN BE WRITTEN AS PRODUCT OF ONE-\( e^- \) WAVEFUNCTIONS

\[
\Psi(r_1, r_2, \ldots, r_N) = \Phi_1(r_1) \Phi_2(r_2) \cdots \Phi_N(r_N) \quad (r_i \text{ ARE COORDS})
\]

FOR \( e^- \neq i \)

THIS FACTORIZATION IS APPROXIMATE BECAUSE MULTI-\( e^- \) \( \hat{A} \) IS NOT SEPARABLE. THIS IS CALLED THE "ORBITAL APPROXIMATION"

* 2ND APPROXIMATION "MEAN-FIELD APPROXIMATION" : ASSUME THAT EACH \( e^- \) MOVES IN A CENTRAL POTENTIAL FIELD OF ALL OTHER \( e^- \) IN THE ATOM (i.e. AN AVERAGE POTENTIAL)

c.a. FOR \( \text{He} \) \( (1s^2) \):

\[
V = \frac{1}{4\pi\epsilon_0} \left( -\frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{|r_1 - r_2|} \right)
\]

DEFINE AVERAGE POTENTIAL:

\[
V_{1\text{eff}}(r_1) = \int d^3r_2 \Phi_2^*(r_2) \frac{1}{r_1 - r_2} \Phi_2(r_2) \quad \text{FOR } e^- \neq 1 \text{ MOVING IN FIELD OF } e^- \neq 2
\]

\[
\left( \frac{e^2}{4\pi\epsilon_0} \right) \left( \frac{Ze^2}{r_1} + \frac{Ze^2}{r_2} \right) - \text{SIMILAR } V_{2\text{eff}}(r_2) \text{ FOR } e^- \neq 2
\]
THIS RADIAL INTEGRATION GIVES A MEAN FIELD USED TO
WRITE A NEW $\hat{H}$ FOR EACH $e^-$:

$$\hat{H}_i (r) = -\frac{\hbar^2}{2m_e} \frac{\nabla^2}{r} + V_{\text{eff}} (r),$$

SIMILAR

FOR $e^-$, $e^-$

($V_{\text{eff}} (r)$ INCLUDES $e^-/e^-$ AND $e^-/\text{NUCLEAR TERMS}$)

THESE TWO APPROXIMATIONS PERMIT US TO KEEP THE IDEA OF
ORBITALS FOR EACH $e^-$, WITH FACTORIZATION OF EACH
ORBITAL INTO SPHERICAL HARMONIC & RADIAL PARTS

$$\chi_j = Y_{\ell m} (\theta, \phi) \rho_j (r)$$

BUT THE RADIAL WAVEFUNCTIONS

ARE NOT THE SAME AS H-ATOM

RADIAL FUNCTIONS

($\text{FOR } e^- j$)

RADIAL FUNCTIONS $\rho_j (r) = \sum_k a_{jk} \chi_k (r)$

EXPANDED IN A BASIS SET OF $e_j$ GAUSSIAN FUNCTIONS $\chi_k (r)$

WITH EXPANSION COEFFICIENT $a_{jk}$ FOR EACH GAUSSIAN FUNCTION

$e^{-r^2/\sigma_k^2}$ - EACH BASIS FUNCTION HAS A DIFFERENT WIDTH.

* THE VALUES OF COEFFICIENTS $a_{jk}$ ARE DETERMINED

USING A VARIATIONAL PRINCIPLE CALCULATION

* AFTER WAVEFUNCTIONS ARE DETERMINED, SLATER DETERMINANT

$(N \times N)$ IS CALCULATED TO ENSURE PAULI PRINCIPLE IS

OBEYED FOR SPIN-ORBITALS

$$\left| \begin{array}{cccc}
\chi_1 (1) & \cdots & \chi_N (1) \\
\vdots & \ddots & \vdots \\
\chi_1 (N) & \cdots & \chi_N (N)
\end{array} \right| \sqrt{N!}$$

HARTREE-FOCK CALCULATIONS ARE DONE ITERATIVELY

IN SOFTWARE PACKAGES.
**Procedure:** (For each $e^-$ in atom)

1. **Begin with H-like radial wavefunction for each $e^-$:** $\psi_i(r_j)$
2. **Put two $e^-$ in each orbital (spin-paired)**
3. **Use product wavefunction of all $e^-$** $i \neq j$ to calculate an $V_{\text{eff}}(r_j)$
4. **Use $V_{\text{eff}}(r_j)$ to solve radial Schrödinger equation for an improved $\psi_j(r)$ with variational calculation**
   $$\psi_j(r) = \Psi_j(r, \theta, \phi) \psi_i(r_j)$$
   $$\frac{-\hbar^2}{2m_e} \frac{\partial^2}{\partial r^2} \Psi_j(r, \theta, \phi) + V_{\text{eff}}(r_j) \Psi_j(r, \theta, \phi) = E_j \Psi_j(r, \theta, \phi)$$

5. **Loop back to step 3 with improved $\psi_j(r_j)$ to calculate $V_{\text{eff}}(r_j)$**
6. **Iterate until no significant changes (decrease) in $E_j$ orbital energies**

"Self-consistent" field refers to the converged mean field.

**General Properties/Results of this approach:**

* HF/SCF method is not exact—does not describe $e^-$ correlation very well, but the energies + wavefunctions agree reasonably well with experimental trends for e.g. ionization energies
  - e.g. He $(1s^2)^+$: $E_{\text{HF}} = -77.9$ eV, $E_{\text{Ion}} = -79.0$ eV

* HF/SCF radial wavefunctions have the same basic shapes & nodal structures as H-orbitals
  - Retain labels with $n, l$ quantum numbers
CHEM 4531 FALL 2015

* HF/SCF APPROACH PROVIDES A BASIS FOR UNDERSTANDING
  THE ORDER OF SPIN-ORBITAL ENERGY LEVELS, AND
  HOW THESE LEVELS ARE POPULATED WITH E- TO FORM
  SPIN-ORBITALS AND ELECTRON CONFIGURATIONS

* WITHIN A SHELL (n) INCREASING l → MORE SPHERICAL
  ORBIT (AS EXPECTED CLASSICALLY) → LESS RADIAL
  PROBABILITY DENSITY AT SMALL r → NUCLEAR CHARGE
  IS BETTER "SCREENED" BY E- FROM INNER SHELLS,
  So E= INCREASES WITH l - UNLIKE H-ATOMS, WHERE
  ENERGIES ONLY DEPEND ON n!

* ENERGIES OF ATOMIC ORBITALS IS APPROXIMATELY EQUAL TO
  NEGATIVE OF THE IONIZATION ENERGIES OF THESE PARTICULAR
  ELECTRONS (ENERGY REQUIRED TO REMOVE E- FROM
  THE ORBITAL) "KOOPMAN'S THEOREM" - THIS
  IS AN APPROXIMATION BECAUSE REMAINING E-
  REARRANGE AFTER IONIZATION
  → SHOW SLIDE WITH IONIZATION TRENDS →

ATOMIC SPECTROSCOPY - USED TO PROBE THE ENERGY
  LEVELS RESULTING FROM E- CONFIGURATIONS

* THE NUMBER & ENERGIES OF ATOMIC ENERGY LEVELS
  ARE SET BY COUPLING BETWEEN ORBITAL ANGULAR
  MOMENTA & ELECTRON SPIN

* APPROXIMATE RULES FOR DETERMINING ELECTRON
  CONFIGURATION OF MULTI-E- ATOMS
  THESE RULES WORK FINE FOR LUN-Z,
  BUT DETAILED CALCULATIONS ARE SOMETIMES
  NEEDED FOR HIGH Z (E.G. LANSTREMAES, ETC.)
1. For a particular shell (value of \( n \)),

\[
\begin{align*}
\gamma_1 &= 2 \quad \text{"L"} \\
\gamma_2 &= 3 \quad \text{"M"} \\
\end{align*}
\]

\( E(\text{s-orbitals}) < E(\text{p-orbitals}) < E(\text{d-orbitals}) \)

\( 1s < 2s < 2p < 3s < 3p < 3d \ldots \)

Sub-shell (\( \ell \)-value) degeneracy lifted in multi-e- atoms

Terminology:

\( \gamma \rightarrow \text{"shell"} \quad \ell \rightarrow \text{"sub-shell"} \)

2. Fill orbitals from lowest to higher energies with \( Z_e^-/\text{orbital} \), \( Z_p+1 \text{ orbitals/sub-shell} \)

\( Z_e^-/\text{s-orbitals} \quad 6e^-/\text{p-orbitals} \quad 10e^-/\text{d-orbitals} \quad \text{etc.} \)

3. If a degenerate set is encountered (same \( \ell \), but different \( m_\ell \)) then first one \( e^-/\text{orbital} \)

Before pairing \( e^- \)

E.g. \( C(Z=6) : 1s^2 \quad 2s^2 \quad 2p_x^1 \quad 2p_y^1 \quad \text{rather than} \quad 1s^2 \quad 2s^2 \quad 2p_x^2 \)

* "Hund's rule" atoms adopt configuration that maximizes # of unpaired \( e^- \)

Spin configuration: \( e^- \) in these subshells have parallel spins (all \( |\uparrow\rangle \) or \( |\downarrow\rangle \)) before pairing up.

The basic reason is that orbitals containing two \( e^- \) are slightly larger than same orbital with one \( e^- \)

\( \rightarrow \) so they have higher potential energy \( \rightarrow \) higher total energy.
Zooming in on the energies of the electronic states in higher resolution, there are multiple states associated with a particular set of \( n, l, m \) values due to interaction with \( s \) and \( ms \) (\( e^- \) spin).

The physical reason for the differing energies of these "spin-orbit" states is that the spin of each electron \( j \) (\( s_j \)) leads to a magnetic dipole moment, which interacts with the magnetic moment associated with its orbital angular momentum \( l \) — the relative orientations of these magnetic moments need to be added, and this term changes the electronic energy levels.

To add \( l \) and \( s \) angular momentum vectors, we need to follow a special procedure for adding Q.M. vectors called the "Clebsch-Gordan" series.

It should be no surprise that since Q.M. \( \vec{l} \) vector has quantized projections onto a fixed axis \( (2l+1) \) that the sum of two \( \vec{l} \) vectors can only take quantized values.

To add two vectors \( j_1 + j_2 \):

\[
J = j_1 + j_2, \quad j_1 + j_2 - 1 \ldots \quad |J - J|_{\text{possible sums}}
\]

\( J \) parallel \( \rightarrow \) \( J \) anti-parallel

\( (\text{max}) \) parallel decrement by 1 \( (\text{min}) \) anti-parallel

e.g. For two \( e^- \) spins, \( s_1 = \frac{1}{2} \quad s_2 = \frac{1}{2} \)

So sum \( S = \frac{1}{2} + \frac{1}{2} \), \( \frac{1}{2} - \frac{1}{2} = 1, 0 \)

only two possible sums
Remember that the total spin states S = 0, 1 have the same properties as usual angular momentum vectors, so e.g.
S = 1 has \( M_S = \pm 1, 0, 1 \) "triplet" spin pair
S = 0 has \( M_S = 0 \) only, "singlet" spin pair

This procedure is also used to calculate the total angular momentum from coupling spin(s) and orbital (l) momenta:
\[
\hat{J} = \hat{L} + \hat{S}, \quad \hat{L} + 1 \ldots |L-S|
\]

So for an electron in a d-orbital, \( S = \frac{1}{2} \)

\[
|L = 2, M_L = \pm 2, M_S = \frac{1}{2} \}
\]

Total spin state of an atom is specified by writing a "term symbol" which depicts the various angular momentum sums:

\[
\begin{align*}
\hat{L} &= \sum_{j=1}^{J} \hat{l}_j, & \text{total orbital angular momentum (2L+1 values of } M_L \text{) capital "M"} \\
\hat{S} &= \sum_{i=1}^{S} \hat{s}_i, & \text{total spin - } 2S+1 \text{ values of } M_S \text{ capital "m"} \\
\hat{J} &= \hat{L} + \hat{S}, & \text{total angular momentum} \\
\end{align*}
\]

Atomic term symbol: \( ^{2S+1}L_J \)

\( \hat{L} + \hat{M} \rightarrow \text{microstates, no need to learn for Pchem} \)
CONSTRUCTING AN ATOMIC TERM SYMBOL:

1. Use Clebsch-Gordon Series to add individual momenta.
2. Letter for total orbital angular momentum of open shells: \( L = 0, 1, 2, 3, 4 \) 
   \[ S, P, D, F, G \]

Closed/filled shells + subshells have \( L = 0, S = 0 \) (no orbital or spin angular momenta)

→ Only valence \( e^- \), unfilled shells need to be considered:
   i.e. \( L(1s^2) = L(2p^6) = 0 \)

Single \( e^- \) in orbital outside closed shell, \( L = \ell \)
   (e.g. \( 1s^2 3p \rightarrow "P" \))

Two \( e^- \) in \( p \)-orbitals (\( \ell = 1 \)) can add to \( L = 2, 1, 0 \)
   \( D, P, S \)

3. Superscript = "multiplicity" of \( e^- \) spin
   Closed shells: (paired spins) \( \rightarrow S = 0 "\text{Singlet}" \)
   e.g. \( ^1S \)
   One \( e^- \): \( (S = \frac{1}{2}) \) \( \rightarrow 2S + 1 = 2 "\text{Doublet}" \) e.g. \( ^2S \)
   Two \( e^- \): \( 2S + 1 = 3 "\text{Triplet}" \) e.g. \( ^3D \)

4. Subscript indicates total angular momentum quantum #: \( J \) tells us the relative orientation of total spin + orbital angular momenta (large \( J \rightarrow \) parallel, small \( J \rightarrow \) anti-parallel)

   e.g. \( 1s^2 3p \)
   \( L = 0 \rightarrow L = 0 "S" \)
   \( S = \frac{1}{2} \rightarrow S = \frac{1}{2} \) \( 2S + 1 = 2 \)
   \( J = L + S = \frac{1}{2} \rightarrow 2S = \frac{1}{2} \)

So, Na ground state electronic configuration has one level
ANOTHER EXAMPLE: K L 3p¹ \( l = 1 \rightarrow l = 1 \rightarrow "p" \)

\[ \text{[Na]} \]
\[ J = L+S = 1+\frac{1}{2} = \frac{3}{2} \text{ or } \frac{1}{2} \]

So \( 2p^{3/2} \) or \( 2p^{1/2} \) two levels

He (1s²) Ground State
\[ l = 0 \rightarrow l = 0 \rightarrow "s" \]

Paired e⁻: \( S = 0 \rightarrow 1S \)
\[ J = L+S = 0 \rightarrow 1S₀ \]

Excited State of C (1s² 2s² 2p¹ 3p¹)

Two open shells/subshells: \( l_1 = l_2 = 1 \)
\[ l_1 + l_2 = 0, 1, 2 \rightarrow S \text{ P D} \]
\[ S_1 = S_2 = \frac{1}{2} \]
\[ S = 1, 0 \rightarrow ZS + 1 = 3, 1 \]
\[ J = L+S : \text{ for } ^3D \rightarrow J = 2+1 \rightarrow 3, 2, 1 \]
\[ J_{min} = |L-S| = 1 \rightarrow ^3D_3, ^3D_2, ^3D_1 \]

For \(^3D \rightarrow J = 2+0 \rightarrow Z \rightarrow ^1D_2 \)

For \(^3P \rightarrow J = 1+1 \rightarrow 2, 1, 0 \rightarrow \)
\[ ^3P_2, ^3P_1, ^3P_0 \]

For \(^1P \rightarrow J = 1+0 \rightarrow 1 \rightarrow ^1P_1 \]

For \(^3S \rightarrow J = 0+1 \rightarrow 1 \rightarrow ^3S_1 \)

For \(^1S \rightarrow J = 0+0 \rightarrow ^1S_0 \)

10 states (seven triplet states, 3 singlets)
**INTRODUCTION TO ATOMIC SPECTROSCOPY**

* Light is absorbed/emitted due to transitions between atomic electronic levels.
* We will only consider single-photon transitions in this class.

\[ \Delta E = \hbar c/\lambda \]

But conservation of energy isn't the only criterion for determining if a transition (1\( \rightarrow \)2 or 2\( \rightarrow \)1) can occur.

"Selection rules" specify which electronic transitions are allowed (i.e. are highly probable) "forbidden" transitions are weak.

**Selection rules for interaction of light's electric field with the transient dipole moment arising from movement of e\textsuperscript{-} charge in atom are consequences of conservation of angular momentum.**

Recall that photons are bosons (spin = 1).

When absorbed/emitted, this momentum is transferred/removed from the atom, requiring a change in angular momentum of the electronic state \((\pm 1/2)\).

The selection rules can be derived quantitatively (we'll get hints in a few weeks) but it's intuitive at least for H- like atoms:

\[ \Delta n \text{ are all allowed} \]
\[ \Delta l = \pm 1 \quad \leftrightarrow \quad p \leftrightarrow d \leftrightarrow f \]
\[ \Delta m_l = \pm 1, 0 \]
FOR MULTI-ELECTRON ATOMS, THE SELECTION RULES ARE:

\( \Delta S = 0 \) (PHOTONS DON'T DIRECTLY AFFECT \( S \))

\( \Delta L = 0, \pm 1 \) BUT \( L=0 \rightarrow L=0 \) NOT ALLOWED

AND \( \Delta \ell = \pm 1 \) FOR AN INDIVIDUAL ELECTRON

\( \Delta J = 0, \pm 1 \) BUT NO \( J=0 \rightarrow J=0 \)

TO USE THESE RULES, LOOK AT BOTH THE TERM SYMBOL AND THE CHANGE IN ELECTRON CONFIGURATION configuration \( \rightarrow \) WHICH ORBITALS ARE INVOLVED

TERM SYMBOL \( \rightarrow \) ANGULAR MOMENyMUM CHANGES

e.g. \( \text{Ar} \) \( \text{(} 1K^3\text{p}^6 \text{;} ^1S_0 \text{)} \rightarrow \text{KL3p}^5\text{4p}^1\text{p} \)

\( \sqrt{\Delta S = 0} \) (SINGLET \( \rightarrow \) SINGLET)

\( \Delta L = +1 \), \( \Delta \ell = 0 \) \( \text{(p} \rightarrow \text{p}) \times \text{NOT ALLOWED} \)

\( \Delta J = +1 \)

e.g. EXCITED-STATE TRANSITION OF \( \text{He} \)

\( \sqrt{\Delta S = 0} \)

\( \sqrt{\Delta L = 0} \), \( \Delta \ell = -1 \) \( \rightarrow \) ALLOWED TRANSITION

\( \sqrt{\Delta J = 0} \)

* THE RULES WE'VE DISCUSSED ARE FOR LIGHT/MEDIUM ATOMS \( (Z < 40) \) FOR HEAVIER ATOMS, THERE IS MORE COUPLING, SO e.g. SINGLET \( \rightarrow \) TRIPLET TRANSITIONS MIGHT OCCUR.

* THESE RULES ARE FOR TRANSITIONS BETWEEN BOUND STATES. TRANSITIONS FROM BOUND STATES \( \rightarrow \) CONTINUUM (i.e. IONIZATION) ARE ALL ALLOWED.
TYPICAL ENERGIES OF ATOMIC TRANSITIONS:

INNER-SHELL C-: K-edge in Na: \( \approx 1 \text{ keV} \)

HEAVY ATOMS e.g., Ru \((Z = 44)\)

\( K = 22.1 \text{ keV} \)  HDD X-RAY

\( L_1 = 3.22 \text{ keV} \)  SOFT X-RAYS

\( L_2 = 2.97 \text{ keV} \)

\( L_3 = 2.84 \text{ keV} \)

OUTER-SHELL C-: \( \text{Na} (Z = 11) 1s^22s^22p^63s^1 \)

VISIBLE PHOTONS

\( ^2S_{1/2} \rightarrow ^2P_{3/2}, \ ^2P_{1/2} \)

\( \approx 589 \text{ nm} \)

17,000 cm\(^{-1}\)  \( (3p \rightarrow 3s \text{ transition observed}) \)

\( 2 \text{ eV} \)

--- POSSIBLE TOPIC -- LINE SHAPES OF ATOMIC TRANSITIONS ---

NOT COVERED IN SILBET, ALBERTO, BAWendi -- 1/2 DAY OF LECTURE 3PM

OTHERWISE -- B.O. APPROXIMATION (CHAP. 11)

* RELATIVE ENERGIES OF VALENCE SHELL TRANSITIONS:

\( \uparrow \)

SINGLET/TRIPLET STATES, PHOSPHORESCENCE

\( \uparrow \)

DEPOLAR BACKscATTERING + NATURAL LINEWIDTHS
LINWIDTHS OF ATOMIC TRANSITIONS (CHEMAGISI)

IN A SPECTROSCOPIC MEASUREMENT, WE CAN MEASURE THE ENERGY/FREQUENCY/WAVELENGTH OF A TRANSITION BETWEEN QUANTUM LEVELS (I.E. WHAT WE'VE MOSTLY BEEN DISCUSSING) BUT ALSO WE CAN RESOLVE THE INTENSITY (I.E. EXTINCTION COEFFICIENT) AND THE LINESHAPE

IF THE EXPERIMENTAL SYSTEM HAS SUFFICIENT RESOLUTION, THEN A LINESHAPE CAN BE MEASURED, WHICH GIVES INFORMATION ON THE DYNAMICS OF THE ABSORBING/EMITTING SPECIES.

LINESHAPE/WIDTHS FOR VIBRATIONAL/ROTATIONAL/ ELECTRONIC TRANSITIONS ARE COMPLICATED AND INFLUENCED BY MANY FACTORS, SOME OF WHICH WE'LL DISCUSS SOON. ATOMIC TRANSITIONS ARE RATHER SIMPLE, HOWEVER, AND THE LINES ARE BROADENED BY TWO CATEGORIES OF EFFECTS, EACH OF WHICH GIVES A DISTINCTIVE SHAPE TO THE LINE.

(A) DOPPLER BROADENING - THIS EFFECT IS OBSERVED IN A GAS WHERE ATOMS ARE MOVING IN A DISTRIBUTION OF SPEEDS (MAXWELL-BOLTZMANN)

\[ P(v) \propto v^2 e^{-mv^2/2kT} \]

WHEN MAXWELLIAN THE ATOM MOVES TOWARDS THE OBSERVER AT A CONSTANT SPEED (I.E. BEFORE COLLISION), THE WAVELENGTH OF A TRANSITION IS COMPRESSED. IN TERMS OF FREQUENCY, THE SHIFT IS

\[ v_+ = \frac{v_0}{1 + \frac{s}{c}} \]

WHERE \( v_0 \) IS FREQ. OF TRANSITION, \( v_+ \) IS FREQ. OF ATOM MOVING TOWARDS OBSERVER

(C IS SPEED OF LIGHT)

AT SPEED \( s \), \( v_- \) IS FREQ. OF ATOM MOVING AWAY FROM OBSERVER
This redshift + blueshift gives rise to a symmetrical distribution of absorption frequencies if the sample is isotropic. The precise form of the lineshape is Gaussian:

$$I(\nu) \propto \exp \left[ -\frac{c^2 (\nu - \nu_0)^2}{2 \nu^2 k_B T} \right]$$

$\nu_0$ is the center frequency (unshifted)

$\nu$ increases with temperature because speed of atoms increases

$$\text{FWHM} = \frac{\nu_0}{2 \sqrt{\ln 2} \cdot k_B T}$$

At $300 \text{ K}$

Doppler broadening can be used to infer the temperature of the gas if it is the dominant mechanism. It is known as a type of "inhomogeneous broadening" because each atom/absorber differs from others.

(B) Lifetime broadening. Even if a sample is cooled to very low temperatures, the atomic transitions are not infinitely sharp. When Doppler broadening is eliminated, the lineshapes change from Gaussian to Lorentzian:

$$I(\nu) = \left[ 1 + \left( \frac{\nu_0 - \nu}{\nu/2} \right)^2 \right]^{-1}$$

Where $\nu_0$ is the center frequency and $\nu$ is the width of the line. This width is related to the lifetime of the transition state being probed:

$$\nu = \left( 5.3 \text{ cm}^{-1} \right)/(2 \text{ ps})$$

States with short lifetimes $\rightarrow$ broad transitions
THE SPECTRAL BROADENING DUE TO FINITE LIFETIME IS A CONSEQUENCE OF THE TIME-DEPENDENT SCHRODINGER EQUATION. ANY SYSTEM THAT IS IN A STATE WITH LIFETIME \( \tau \) HAS AN ENERGETIC BROADENING OF THE STATE \( \Delta E = \hbar / \tau \).

THIS IS NOT AN UNCERTAINTY PRINCIPLE DUE TO TIME/ENERGY NOT BEING COMPLEMENTARY OBSERVABLES (TIME IS A PARAMETER IN Q.M., NOT AN OBSERVABLE).

WHY DO ATOMIC LEVELS (EXCITED STATES) HAVE FINITE LIFETIMES? TWO EFFECTS:

1. COLLISIONAL DEACTIVATION - IF EXCITED SPECIES COLLIDE WITH GROUND-STATE ATOM OR MOLECULES, THE LEVEL WILL BE BROADENED. THIS CONTRIBUTION CAN BE MINIMIZED @ LOW PRESSURE.

2. NATURAL WIDENING - ANY EXCITED STATE CAN DECAY BY EMISSION OF A PHOTON (FLUORESCENCE). THIS SPONTANEOUS EMISSION TYPICALLY OCCURS ON A NS \((10^{-9}\text{ sec})\) TIMESCALE FOR ATOMIC TRANSITIONS, AND IS CAUSED BY COUPLING TO FlUCTUATIONS OF THE QUANTIZED ELECTROMAGNETIC FIELD (QUANTUM ELECTRODYNAMICS).

LIFETIME BROADENING IS KNOWN AS "HOMOGENEOUS" - SAME FOR ALL ATOMS.
From atoms to molecules - Q.M. Basis for Chemical Bonding (Chapter 11)

The simplest molecule we can consider is $\text{H}_2^+$

2 nuclei and one $\text{e}^-$.

$\text{e}^-$ is located at $\Gamma$; $\Gamma$ from $\text{H}_A$ etc.

$\text{H}_A$ is located at $R_A$; $\text{H}_B$ @ $R_B$

Hamiltonian is

$$\hat{H} = -\frac{\hbar^2}{2m_e} \frac{d^2}{d\Gamma^2} - \frac{\hbar^2}{2m_A} \frac{d^2}{dR_A^2} - \frac{\hbar^2}{2m_B} \frac{d^2}{dR_B^2} - \frac{\text{e}^2}{4\pi\varepsilon_0} \left( \frac{1}{|R_A - \Gamma|} + \frac{1}{|R_B - \Gamma|} \right)$$

$\text{h}^2/k_e$ \quad $\text{H}_A$ k.e. \quad $\text{H}_B$ k.e. \quad $\text{e}^-/\text{H}_A$ \quad $\text{e}^-/\text{H}_B$

$\text{H}_A - \text{H}_B$ Repulsion

3-body problem

This Hamiltonian is not separable $\neq H(\Gamma) + H(R)$

Recall that $m_e \approx 10^{-31}$ kg, $m_{\text{H}_2^+} \approx 10^{-27}$ kg.

So electrons typically move much faster than nuclei.

From perspective of $\text{e}^-$, nuclei are almost fixed in space (mosquitoes buzzing around a person)

So $\text{e}^-$ experience a static field defined by the nuclear geometry (bond length, $R$)

Two simplifications of $\hat{H}$ follow by making a "clamped-nucleus" approximation

1. Nuclear kinetic energies $\rightarrow 0$

2. Replace operators $\hat{R}_A \hat{R}_B$ with parameters $R_A$, $R_B$

$\Rightarrow$ "Born-Oppenheimer" approximation
CHEM 4531  FALL 2015  B.O.  APPROXIMATION

SIMPLIFIED $\hat{H}$:

$$\hat{H}_B (R_A, R_B) = -\frac{\hbar^2}{2m_e} \nabla^2 + \frac{e^2}{4\pi\varepsilon_0} \left[ \frac{1}{|R_A-\mathbf{r}|} + \frac{1}{|R_B-\mathbf{r}|} - \frac{1}{R} \right]$$

$V_{\text{eff}}$ depends only on position of $e^-$ within nuclear geometry.

So we can write:

$$\hat{H}_B (R_A, R_B) = -\frac{\hbar^2}{2m_e} \nabla^2 + V_{\text{eff}} (R_A, R_B) + \frac{e^2}{4\pi\varepsilon_0 R}$$

* In this picture, $e^-$ move on an electronic potential energy surface - $e^-$ and nuclear motions are now separated!

$V_{\text{eff}}$

* It is assumed that $e^-$ quickly adjust to changes in nuclear geometry ($R$)

In general, for nuclear coordinates $Q_x$ and $e^-$ coordinates $q_i$, the total $e^-$/nuclear problem is solved.

1. Solve time-independent Schrödinger eq. for $\psi_i (Q_x, q_i)$

   $\rightarrow$ electronic wavefunction for each nuclear separation

   $\rightarrow$ electronic eigenvalues $E_{n_e} (Q_x) = U_{\text{nuc}} (Q_x)$

   $\hat{0}(Q) = U_{\text{nuc}} (Q_x) + V_{\text{nuc-nuc}}$ is the potential energy function on which nuclei move

2. Solve T.I.S.E. for nuclear motion $\psi_{\text{nuc}} (Q_x)$

   With total $\hat{H}_{\text{nuc}} = \hat{T}_{\text{nuc}} + \hat{0}(Q) \rightarrow$ nuclear wave functions
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THOSE NUCLEAR WAVEFUNCTIONS DESCRIBE MOLECULAR VIBRATIONS & ROTATIONS

3. TOTAL : $\Psi_{\text{TOTAL}} = \Psi_2 (Q_1, Q_2) \Psi_{\text{NUC}} (Q_2)$
   IS A PRODUCT

\[ \text{Now, let's use the Born-Oppenheimer approximation to examine } H_2^+ \text{ molecular ion - } H_A \cdot H_B \text{ (two protons) sharing an } e^- \]

\[ \text{If } R \text{ is large (} > 0.53 \text{ Å)} \text{, we expect to see two possible configurations (ground state):} \]

\[ |1s_A\rangle \quad \text{e}^- \text{ near proton } A \]
\[ |1s_B\rangle \quad \text{e}^- \text{ near proton } B \]

\[ \text{So it's reasonable to think the total wavefunction of this system will be the linear combination of atomic orbitals (LCAO)} \]
\[ |\Psi\rangle = c_1 |1s_A\rangle + c_2 |1s_B\rangle \]

\[ \text{For this homonuclear diatomic } \rightarrow c_1 = c_2 \]

\[ \text{We would like to calculate the binding energy:} \]
\[ \Delta E = \frac{\langle \Psi_+ | H_{\text{EO}} | \Psi_+ \rangle}{\langle \Psi_+ | \Psi_+ \rangle} \]

\[ \text{Remember that } |1s\rangle \propto e^{-2 r/\alpha} \]
\[ \text{Exponential decay of } e^- \text{ density} \]

\[ \text{Let's consider how these LCAO wavefunctions look, and if they result in a stable } H_2^+ \text{ molecule.} \]
* **H₂⁺ BONDING**

* Two bare protons will repel each other
* electrostatic interaction will screen nuclear repulsion
* increased electron density between nuclei is therefore expected to result in lower energy compared to \( \text{H}^+ / \text{H}^- \) pair, so

\[
\Delta E_\text{e} (R) = \frac{J(R) \pm K(R)}{1 \pm S(R)}
\]

* \( S(R) = \langle 1S_A | 1S_B \rangle \) is the "overlap integral"

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* \( J(R) = \langle 1S_A | H | 1S_B \rangle = e^{-R} (1 + \frac{1}{R}) \) for \( \text{H}_2^+ \)
* \( K(R) = \langle 1S_A | \hat{H} | 1S_B \rangle = \frac{e^{-R}}{R} - e^{-R} (1 + \frac{1}{R}) \)

* The field of the other nucleus "Coulomb integral"

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* **Resonance Integral** or **Exchange Integral**

* No classical description - kind of like a measure of attraction between a nucleus and the \( \text{e}^- \) density in the internuclear region "\( \text{e}^- \) sharing"
**H$_2^+$ Bonding**

These integrals are all a function of $R$ - so we can calculate potential energy curves:

$$ V = V_{\text{electron}} + V_{\text{nn}} = E_+ (R) + V_{\text{nn}} (R) $$

The curve for the (+) combination has a minimum → stable bond is formed.

Curve for the (-) combination shows exponential decay from large value $> 0$ → repulsive potential.

$$ |\psi_+\rangle = \frac{|1s_A\rangle + |1s_B\rangle}{\sqrt{2(1+5)}} \rightarrow "\text{bonding orbital}" $$

$$ |\psi_-\rangle = \frac{|1s_A\rangle - |1s_B\rangle}{\sqrt{2(1-5)}} \rightarrow "\text{anti-bonding orbital}" $$

**Correlation Diagram**

![Diagram showing correlation between orbitals $1s_A$ and $1s_B$ and the wave function $\psi_+$ and $\psi_-$]  

* The resonance/exchange integral $K(R)$ is the most important term for chemical bonding → $\psi$ "sharing."

* Stable bond is formed when screening of nuclear repulsion by bonding: $\psi$ lowers energy of $\psi_+$ compared to $|1s_A\rangle \langle 1s_B|$.

* The simple trial $\psi_+$ discussed here, with $1s$ orbitals only gives about 50% of the expected bonding energy. For better approximation:

$$ \psi = c_1 |1s_A\rangle + c_{15} |1s_B\rangle + c_5 |2s_A\rangle + c_4 |2s_B\rangle + c_5 |2p_{2,z}\rangle $$

$P_z$ orbitals along internuclear axis.
NOW THAT THE ELECTRONIC PROBLEM IS SOLVED, WE CAN USE THE POTENTIAL ENERGY CURVE TO FIND THE WAVEFUNCTION FOR NUCLEAR MOTION

\[ \psi_{\text{total}} = \psi_{\text{electronic}} \times \psi_{\text{nuclear}} \]

NEAR THE MINIMUM, WE CAN OFTEN DESCRIBE THE POTENTIAL AS PARABOLIC (i.e., HARMONIC)

\[ \rightarrow \psi_{\text{nuclear}} \text{ ARE HARMONIC OSCILLATOR WAVEFUNCTIONS} \]

THIS LCAO TREATMENT CAN BE EXTENDED...

E.g., FOR NON-NUCLEAR DISTANCES

AT LARGE SEPARATIONS, ATOMIC ORBITALS (e.g., 1s 2s 2p...)

@ SHORT DISTANCES, "MOLECULAR ORBITALS" = LCAOS

DESCRIBE MIXING OF ATOMIC STATES:

\[ \psi = \sum_{i=1}^{N} c_i \phi_{i,A} + \sum_{j=1}^{N} c_j \phi_{j,B} \]

SIMILAR ATOMIC ORBITALS (i.e., LARGE OVERLAP \( \langle \phi_A | \phi_B \rangle \))

WILL BE STRONGLY MIXED \( \rightarrow \) CONTRIBUTE TO BONDING

VARIATIONAL APPROACH WITH \( c_i, c_j \) AS PARAMETERS USED TO OBTAIN MINIMUM ENERGIES

IT SO HAPPENS THAT FOR CASE JUST DISCUSSED, \( \psi^+ \) LCAO IS A SYMMETRIC, BONDING ORBITAL AND \( \psi^- \) LCAO IS AN ANTISYMMETRIC, ANTI-BONDING ORBITAL

\( \star \) THIS IS NOT A GENERAL RULE!

GENERAL RULE: BONDING ORBITALS \( \rightarrow \) CONSTRUCTIVE INTERFERENCE

ANTI-BONDING \( \rightarrow \) NODES OF \( \psi^- \)

DENSOITY BETWEEN NUCLEI

GIVEN THE \( \psi^+ \) AND \( \psi^- \) "MOLECULAR ORBITALS" WE DETERMINE THE MOLECULAR ELECTRONIC CONFIGURATION BY PLACING \( \psi^- \) IN ORBITALS & COMPLYING W/ PAULI PRINCIPLE
Chem 4531 Fall 2015
Chemical Bonding (Diatomic)

\( \text{H}_2^+ \text{ only has one } e^- \rightarrow \text{ goes into } \psi_+ \text{ state} \)

\( \text{H}_2 \text{ has two } e^- \text{ so they can both go into } \psi_+ \)

\text{and spin-pair to ensure antisymmetry:}

Slater determinant

\[ \psi_+ = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_+(1) \alpha(1) & \psi_+(2) \beta(1) \\ \psi_+(2) \alpha(2) & \psi_+(2) \beta(2) \end{vmatrix} \]

\[ \psi_+ = \frac{1}{\sqrt{2}} \psi_+(1) \psi_+(2) \left[ \alpha(1) \beta(2) - \alpha(2) \beta(1) \right] \]

Which is a description of this diagram:

\[ \begin{array}{c} 1s_a \\ \downarrow \end{array} \quad \begin{array}{c} \psi_+ \\ \downarrow \end{array} \quad \begin{array}{c} 1s_b \end{array} \]

So far, I labeled the molecular orbitals "\( \psi_+ \)" and "\( \psi_- \)"

There is a system for describing MOs which is analogous to classification of atomic orbitals

In atoms, we label \( 1s, 2p, \ldots \)

MOs for diatomics:

1. Label basis orbital (e.g., 1s)
2. \( \lambda \) (angular momentum onto bond axis)
   \[ \lambda = \pm \frac{\alpha}{2} \quad \alpha, \pi, \sigma, \ldots \]
3. Bonding or antibonding (*)
4. Parity (u or g) odd/even

Constructing MO labels:

1. Add atomic orbitals. Colors/signs represent sign of wavefunction amplitude
2. \(+/-\) and \(-/-\) → constructive interference
3. \(+/-\) → destructive interference

Examples:

\[ \begin{array}{c} 1s \\ \downarrow \end{array} \quad \begin{array}{c} 1s \\ \downarrow \end{array} \quad \begin{array}{c} \otimes \quad \ominus \quad 0^* \text{ (1s)} \end{array} \quad \text{anti-bonding} \]

\[ \begin{array}{c} (+) \quad (+) \\ \downarrow \quad \downarrow \end{array} \quad \begin{array}{c} \oplus \quad \oplus \quad 0^b \text{ (1s)} \end{array} \quad \text{bonding} \]

Cylindrical symmetry about bond axis → "\( \sigma \)"
HEM 4531 FALL 2015 DIATOMICS / ORBITALS

SIMILAR FOR ZS A.O.S. \( \rightarrow \) \( \sigma_g (ZS) + \sigma_u^* (ZS) \)

\[ \begin{array}{c}
\infty \pm \infty \\
\rightarrow \\
\infty \infty \\
\rightarrow \\
\end{array} \]

\( \sigma_u^* (Zp) \) \( \gamma \) BONDING

\[ \begin{array}{c}
\infty \pm \infty \\
\rightarrow \\
\infty \infty \\
\rightarrow \\
\end{array} \]

\( \sigma_g (Zp) \) \( \gamma \) ANTI-BONDING

\( \pi \pm \pi \)

\[ \begin{array}{c}
\infty \pm \infty \\
\rightarrow \\
\infty \infty \\
\rightarrow \\
\end{array} \]

\( \pi_u (Zp) \)

\( \gamma \) ANTI-BONDING

\[ \begin{array}{c}
\infty \pm \infty \\
\rightarrow \\
\infty \infty \\
\rightarrow \\
\end{array} \]

\( \pi^* (Zp) \)

\( \gamma \) BONDING

\( \gamma \) NO nodes BETWEEN NUCLEI

\( \gamma \) NO NODAL PLANE Cp

\( \gamma \) TO BOND AXIS

NOW, WE CAN PROPERLY LABEL THE MOLECULAR ORBITAL DIAGRAM FOR \( H_2 \):

\[ \begin{array}{c}
\infty \pm \infty \\
\rightarrow \\
\infty \infty \\
\rightarrow \\
\end{array} \]

\( \sigma_u^* (15) \)

CONCEPT OF BOND STRENGTH "BOND ORDER"

\[ \text{Bond Order} = \frac{1}{2} \left[ \frac{\text{(\# of } e^- \text{ in bonding orbitals)}}{\text{(\# of } e^- \text{ in anti-bonding orbitals)}} \right] \]

So this diagram explains why \( H_2 \) has a stronger bond than \( H_2^+ \)

\begin{align*}
\text{Bond} & \quad R & D_0 & \nu_0 \\
H_2^+ & \frac{1}{2} & 106 \text{ pm} & 2.65 \text{ eV} & 2322 \text{ cm}^{-1} \\
H_2 & 1 & 74 \text{ pm} & 4.98 \text{ eV} & 4400 \text{ cm}^{-1} \\
\end{align*}

S.A.B. READ UP TO 11.5 \( \gamma \) 413 -> (4TH EDITION)

NO NEED TO LEARN UNITED ATOM APPROACH