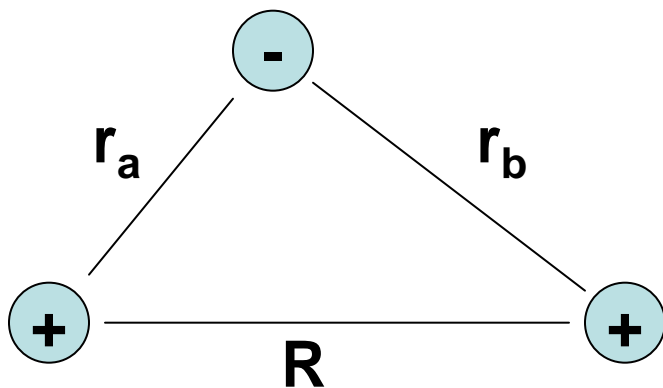
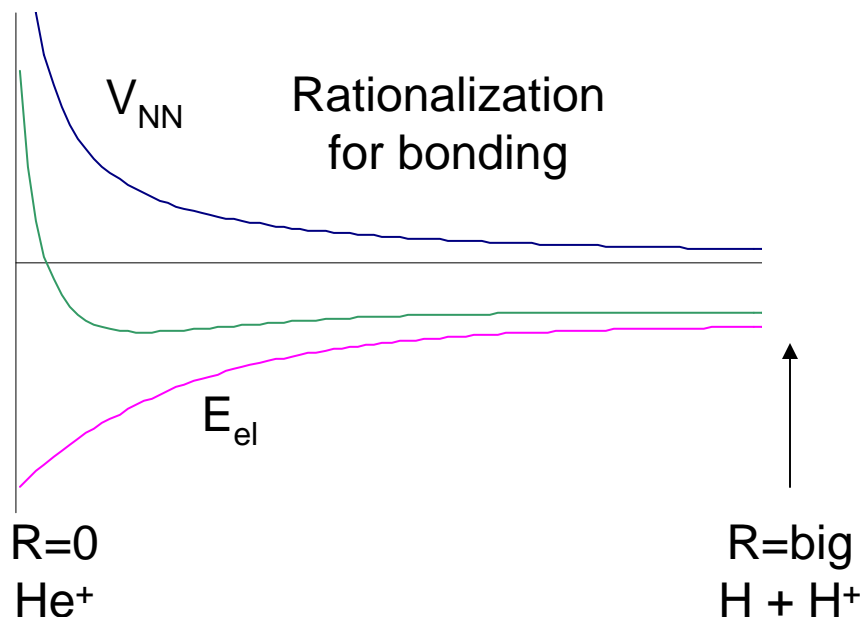


H_2^+ : A Model System for Understanding Chemical Bonds



The first issue we have to deal with is the multiple nuclei; now we can have nuclear vibrations and rotations for the first time. **Important digression: Born-Oppenheimer approximation.**



Overall potential can be rationalized in terms of competition between 1) internuclear repulsion, which blows up as R decreases, and 2) the purely electronic energy, which is more favorable as R decreases.

General Molecular Hamiltonian

$$\hat{H} = \hat{T}_N + \hat{T}_e + V_{NN} + V_{Ne} + V_{ee}$$

Kinetic

$$\hat{T}_N = -\frac{\hbar^2}{2} \sum_{\alpha} \frac{1}{m_{\alpha}} \nabla_{\alpha}^2$$

$$\hat{T}_e = -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2$$

Potential

$$V_{NN} = e^2 \sum_{\alpha} \sum_{\beta > \alpha} \frac{Z_{\alpha} Z_{\beta}}{r_{\alpha\beta}}$$

$$V_{Ne} = -e^2 \sum_{\alpha} \sum_i \frac{Z_{\alpha}}{r_{i\alpha}}$$

$$V_{ee} = e^2 \sum_i \sum_{j > i} \frac{1}{r_{ij}}$$

N = “nuclear”; e = “electronic”

i, j = indices over electrons

α, β = indices over nuclei

Z = nuclear charges

Born-Oppenheimer Approximation

$$\hat{H} = \hat{T}_N + \hat{T}_e + V_{NN} + \underbrace{V_{Ne}}_{\text{troublesome}} + V_{ee}$$

This term is troublesome because it couples electron motion to nuclear motion. Without it, we could solve for nuclear eigenfunctions and electronic eigenfunctions independently.

- The Born-Oppenheimer approximation invokes an *adiabatic* separation of the nuclear and electronic motions, on the basis of the large difference in mass between nuclei and electrons.
- Classically you can envision that the nuclei move much slower than the electrons, such that the electronic degrees of freedom “instantaneously” adjust to the nuclear positions.
- Operationally, we make the electronic Hamiltonian *parametrically* dependent on nuclear positions.

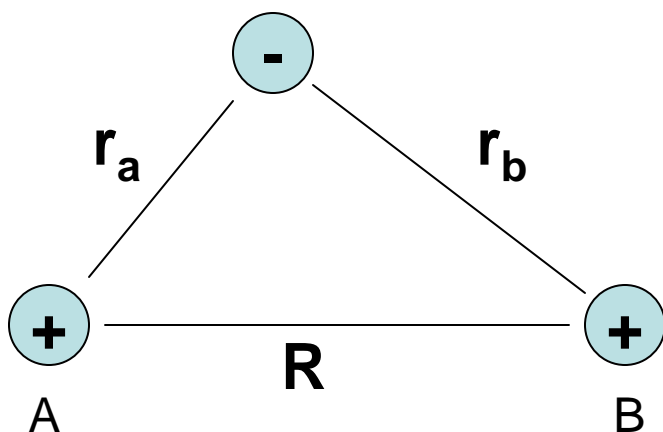
Born-Oppenheimer Approximation, cont'd

$$\hat{H}_e^{eff}(\vec{r}_\alpha) = -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 - e^2 \sum_\alpha \sum_i \frac{Z_\alpha}{r_{i\alpha}} + e^2 \sum_i \sum_j \frac{1}{r_{ij}} + V_{NN}$$

- This approximation underlies the entire concept of “potential energy surfaces”, and by extension, force fields (any time you associate a single energy with a given nuclear configuration).
- Other adiabatic approximations separate vibrations from rotations.
- Important breakdowns of the BO approximation include internal conversion and intersystem crossing (radiationless transitions important in photochemistry).

This can be added in because it's a constant for fixed nuclear positions.

Back to H_2^+



$$\hat{H}_e = -\frac{\hbar^2}{2m_e} \nabla^2 - \frac{e^2}{r_a} - \frac{e^2}{r_b}$$

It turns out that there are analytical solutions, obtained in “confocal elliptic” coordinates:

$$z_1 = \frac{r_a + r_b}{R} \quad (1 \leq z_1 \leq \infty)$$

$$z_2 = \frac{r_a - r_b}{R} \quad (-1 \leq z_2 \leq 1)$$

ϕ = angle around internuclear axis

As you might imagine, the derivation is complex, and in any case, this is not a general method. Instead, let's approach this as a variational problem.

Variational Treatment of H_2^+

As a trial wavefunction, let's use something very simple, specifically a sum of 1s orbitals centered around each nucleus (this fits with our intuition about bonding arising from orbital overlap):

$$\psi = c_A \psi_A + c_B \psi_B$$

ψ_A = 1s orbital centered on nucleus A

ψ_B = 1s orbital centered on nucleus B

c = coefficients to be determined

The secular determinant is

$$\begin{vmatrix} H_{AA} - ES_{AA} & H_{AB} - ES_{AB} \\ H_{BA} - ES_{BA} & H_{BB} - ES_{BB} \end{vmatrix} = \begin{aligned} H_{AA} &= \int \psi_A \hat{H} \psi_A = \int \psi_B \hat{H} \psi_B = H_{BB} \\ H_{AB} &= \int \psi_A \hat{H} \psi_B = \int \psi_B \hat{H} \psi_A = H_{BA} \\ S &= S_{AB} = S_{BA} = \int \psi_A \psi_B \\ S_{AA} &= S_{BB} = 1 \end{aligned}$$
$$\begin{vmatrix} H_{AA} - E & H_{AB} - ES \\ H_{AB} - ES & H_{AA} - E \end{vmatrix} = 0$$

A Closer Look at the Integrals

$$\begin{aligned} H_{AA} &= \int \psi_A \hat{H} \psi_A \\ &= \int \psi_A \left(-\frac{\hbar^2}{2m_e} \nabla_e^2 - \frac{e^2}{r_a} - \frac{e^2}{r_b} \right) \psi_A \\ &= \int \psi_A \left(-\frac{\hbar^2}{2m_e} \nabla_e^2 - \frac{e^2}{r_a} \right) \psi_A - e^2 \int \psi_A \frac{1}{r_b} \psi_A \\ &= \int \psi_A \hat{H}_A^0 \psi_A - e^2 \int \psi_A \frac{1}{r_b} \psi_A \\ &= E_0 - e^2 \int \psi_A \frac{1}{r_b} \psi_A \\ &= E_0 - J \end{aligned}$$

This is just the Hamiltonian for a H atom centered on A, and thus ψ_A is an eigenfunction of it.

These types of integrals are referred to as “Coulomb” integrals, and together with “exchange” integrals (next slide), play a very important role in electronic structure calculations.

A Closer Look at the Integrals (2)

$$\begin{aligned}
 H_{AB} &= \int \psi_A \hat{H} \psi_B \\
 &= \int \psi_A \left(-\frac{\hbar^2}{2m_e} \nabla_e^2 - \frac{e^2}{r_a} - \frac{e^2}{r_b} \right) \psi_B \\
 &= \int \psi_A \left(-\frac{\hbar^2}{2m_e} \nabla_e^2 - \frac{e^2}{r_b} \right) \psi_B - e^2 \int \psi_A \frac{1}{r_a} \psi_B \\
 &= \int \psi_A \hat{H}_B^0 \psi_B - e^2 \int \psi_A \frac{1}{r_a} \psi_B \\
 &= E_0 \int \psi_A \psi_B - e^2 \int \psi_A \frac{1}{r_a} \psi_B \\
 &= SE_0 - K
 \end{aligned}$$

This is just the Hamiltonian for a H atom centered on B, and thus ψ_B is an eigenfunction of it.

This is an “exchange” integral.

We Can Now Solve Secular Determinant

$$E_{\pm} = \frac{H_{AA} \pm H_{AB}}{1 \pm S} = E_0 + \frac{J \pm K}{1 \pm S}$$

**These terms
really give rise
to bonding.**

$$\psi_{\pm} = \frac{1}{\sqrt{2(1 \pm S)}} (\psi_A \pm \psi_B)$$

We've expressed the eigenstates in terms of three types of integrals: overlap, Coulomb, and exchange. These implicitly depend on R , the internuclear distance. For H_2^+ , these turn out to be analytical:

$$J = e^{-2R} \left(1 + \frac{1}{R} \right)$$

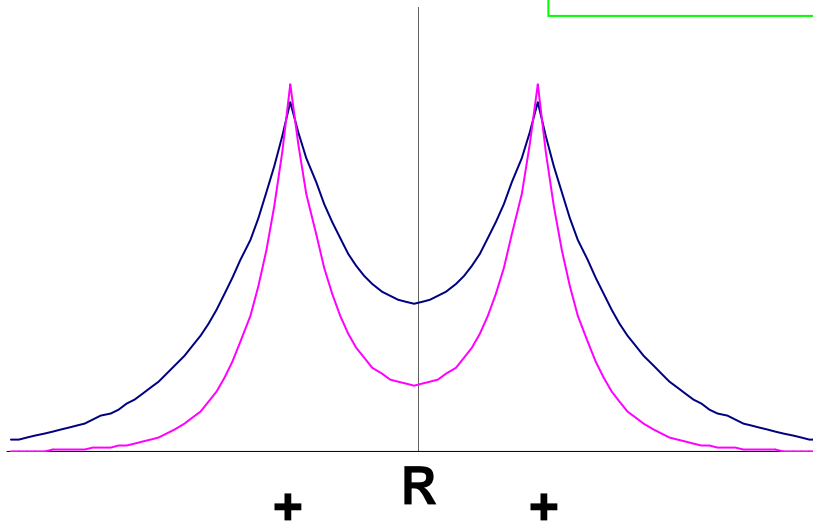
$$K = e^{-R} (1 + R)$$

$$S = e^{-R} \left(1 + R + \frac{R^2}{3} \right)$$

H_2^+ Eigenfunctions

σ_g

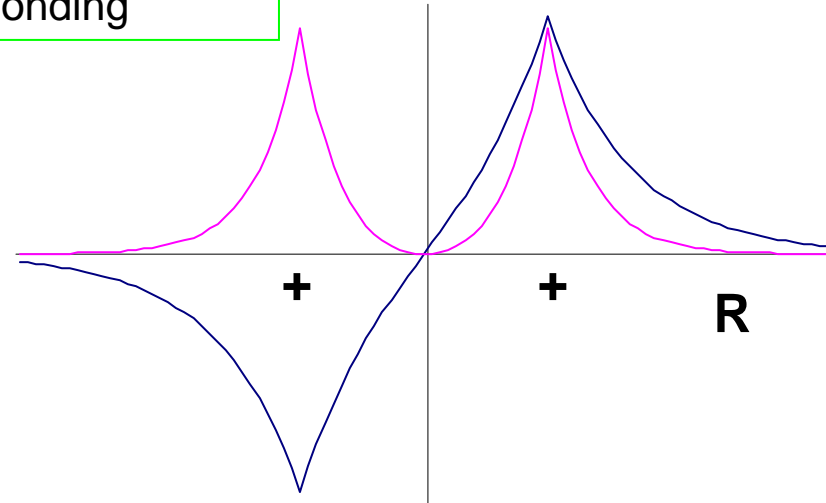
σ = no nodes along ϕ angle
 g/u = symmetry wrt inversion
 $*$ = antibonding



$$\psi_+ = \frac{1}{\sqrt{2(1+S)}} (\psi_A + \psi_B)$$

“Bonding” molecular orbital
 Enhanced electron density in internuclear area, helping to screen protons from each other.

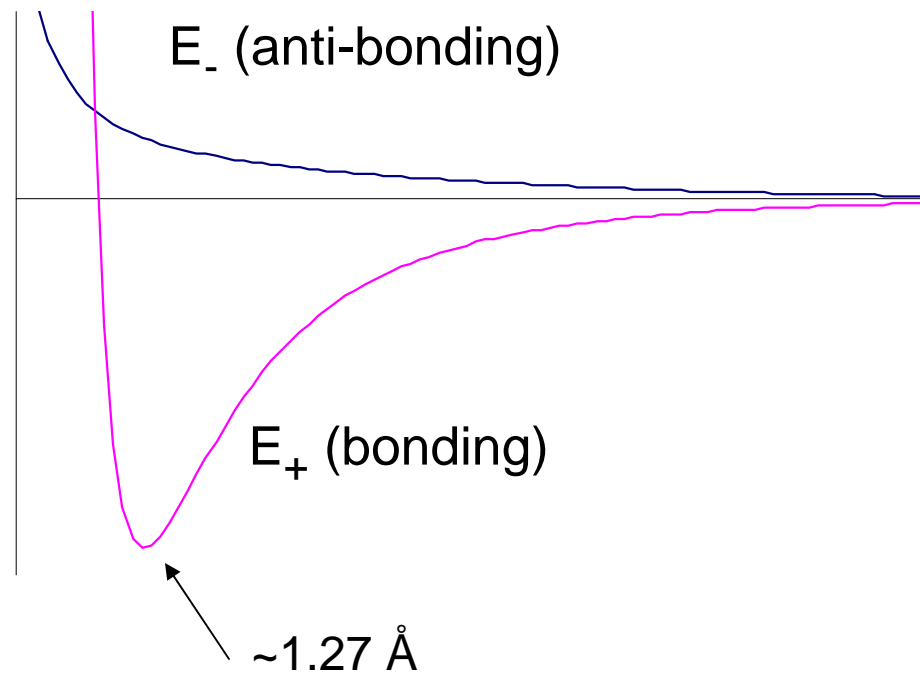
σ_u^*



$$\psi_- = \frac{1}{\sqrt{2(1-S)}} (\psi_A - \psi_B)$$

“Anti-Bonding” molecular orbital
 Depleted electron density in internuclear area, deshielding the protons from each other.

H_2^+ Eigenenergies (Potential Energy Curves)



Was this all a waste of time?

Notice that the wavefunctions do not involve J or K , the Coulomb and exchange integrals:

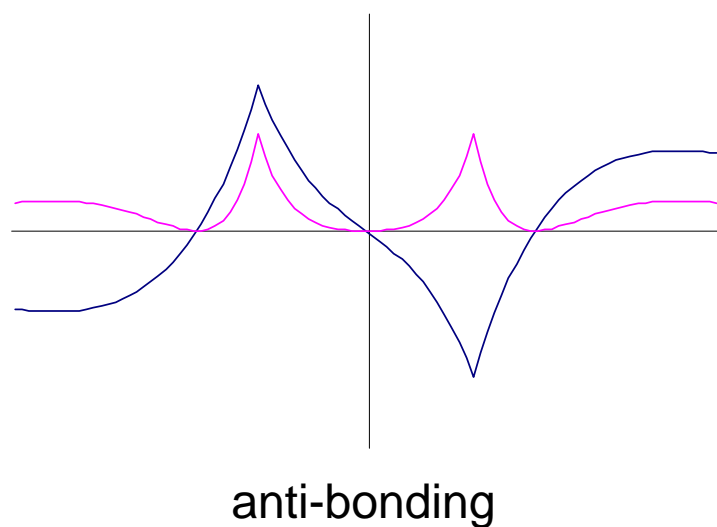
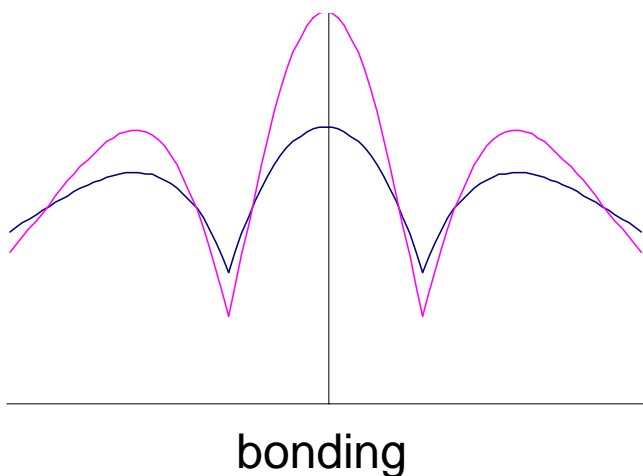
$$\psi_{\pm} = \frac{1}{\sqrt{2(1 \pm S)}} (\psi_A \pm \psi_B)$$

In fact, the form of the wavefunctions is dictated by the symmetry of the problem (remember the symmetric double well potential?). So we didn't really have to invoke the variational method at all to solve for these eigenfunctions.

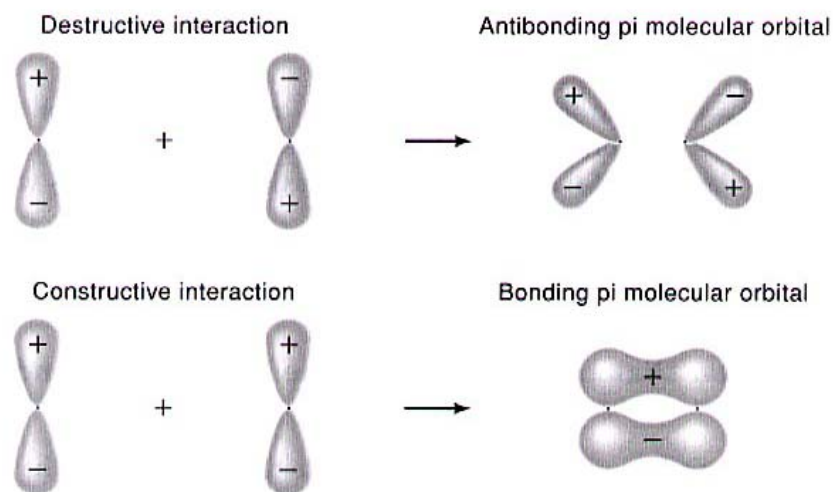
However, the expressions we got for the eigenenergies are non-trivial, and give a feeling for how electronic structure problems are solved in general, as we will see.

H_2^+ Excited States

Example: Mixing “ p_z ” orbitals



Example: Mixing “ $p_{x/y}$ ” orbitals



These are the π orbitals.

These molecular orbitals are familiar, but they can all be calculated quantitatively using the same variational treatment as for the ground state.

Molecular Orbital Diagram

H_2^+ really provides the foundation for the molecular orbital approach to electronic structure.

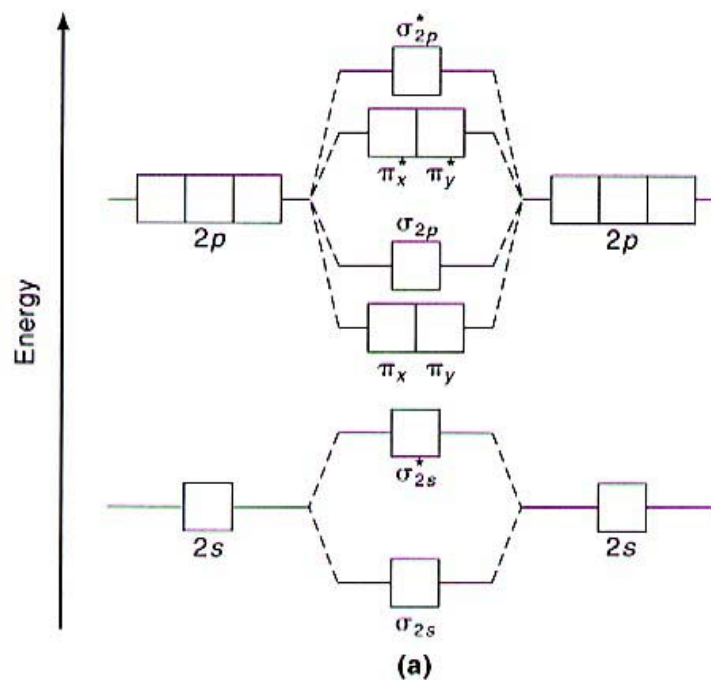


Figure 15.17

Multi-Electron Systems

- No multi-electron system can be solved analytically.
- We will build up our intuition with these model systems:
 - He: building up to multi-electron atoms
 - H₂: first real molecule
- Inter-electron repulsion is the biggest challenge.
- Also need to deal with electron spin: Pauli principle.

Pauli Principle

- Identical particles are “indistinguishable” in quantum mechanics.
- Exchanging particles changes the wavefunction, at most, by a sign change (i.e., applying permutation twice must return you to original wavefunction).

$$\hat{P}_{12}\hat{P}_{12}\psi(\vec{r}_1, \vec{r}_2) = \hat{P}_{12} \pm \psi(\vec{r}_2, \vec{r}_1) = \psi(\vec{r}_1, \vec{r}_2)$$

- Sub-atomic particles have a property called spin, which is an intrinsic angular momentum which can have either integer or half-integer values.
- THERE IS NO CLASSICAL ANALOG OF SPIN; it is a purely QM property. People sometimes imagine the particles like little tops, spinning about an axis, but this is a highly imperfect analogy.
- Particles with integer spin are called bosons; interchanging these gives no sign change of wavefunction.
- Particles with half-integer spin (electrons are important example) are fermions; interchanging these does change sign of wavefunction.

Pauli Principle and 2 Electron Systems

$$\hat{P}_{12}\psi(\vec{r}_1, \vec{r}_2) = -\psi(\vec{r}_2, \vec{r}_1)$$

$$\text{If } \vec{r}_1 = \vec{r}_2 = \vec{r}$$

$$\psi(\vec{r}, \vec{r}) = -\psi(\vec{r}, \vec{r})$$

This can only be the case if the wavefunction is zero. Conclusion: There is zero probability that 2 electrons can be simultaneously found in the same place. This is one of the more common definitions of the Pauli principle; however, as we've seen, it's more general (and also more abstract) in reality.

Pauli Principle and 2 Electron Systems (cont'd)

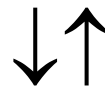
Electrons have spin angular momentum of $J=1/2$. This angular momentum is similar to our treatment of angular momentum of the H atom (i.e., electron rotating around the nucleus), except that the total angular momentum can take half-integer values for spin. By analogy, there are 2 possible values of the “m” quantum number, $m=\pm 1/2$.

4 possible spin states:

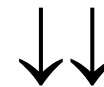
$$\alpha(1)\alpha(2)$$



$$\alpha(1)\beta(2) \quad \beta(1)\alpha(2)$$



$$\beta(1)\beta(2)$$



These do not obey
indistinguishability; symmetrize!

α : $m=+1/2$ (“spin up”)
 β : $m=-1/2$ (“spin down”)

This “normalization constant” ensures that the square of the wavefunction “integrates” to 1 (here the integration is not over physical space, but over the spin “coordinate”).

$$\frac{1}{\sqrt{2}} [\alpha(1)\beta(2) \pm \beta(1)\alpha(2)]$$

$$\uparrow\downarrow \pm \downarrow\uparrow$$

Now let's apply the permutation operator to these ...

$$\hat{P}_{12}\alpha(1)\alpha(2) = \alpha(1)\alpha(2) \quad \uparrow\uparrow$$

$$\hat{P}_{12}\beta(1)\beta(2) = \beta(1)\beta(2) \quad \downarrow\downarrow$$

$$\hat{P}_{12} \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) + \beta(1)\alpha(2)] = \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) + \beta(1)\alpha(2)] \quad \uparrow\downarrow + \downarrow\uparrow$$

$$\hat{P}_{12} \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \beta(1)\alpha(2)] = -\frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \beta(1)\alpha(2)] \quad \uparrow\downarrow - \downarrow\uparrow$$

These 3 spin states are symmetric with respect to electron exchange.

This single spin state is anti-symmetric with respect to electron exchange.

Pauli Principle Applied to He

The ground state of He has both electrons in the “1s” orbital:

$$1s(1)1s(2)$$

This is symmetric with respect to exchange

$$\hat{P}_{12} 1s(1)1s(2) = 1s(1)1s(2)$$

and thus, by itself, does not obey the Pauli principle. However, the complete wavefunction consists of both the orbital (spatial) wavefunction and the spin wavefunction. To obtain a wavefunction that obeys the Pauli principle, there is only one spin wavefunction possible (the anti-symmetric one):

$$\psi_{ground} = 1s(1)1s(2) \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

$$\hat{P}_{12} \psi_{ground} = -\psi_{ground}$$

Pauli Principle Applied to He (cont'd)

What about an excited state of He where one electron is promoted to the 2s orbital:

$$1s(1)2s(2)$$

To obey indistinguishability, must symmetrize

$$\frac{1}{\sqrt{2}} [1s(1)2s(2) \pm 2s(1)1s(2)]$$

The “+” combination must combine with the anti-symmetric spin state, and the “-” combo with the symmetric spin states, to obey Pauli principle:

$$\frac{1}{2} [1s(1)2s(2) - 2s(1)1s(2)] [\alpha(1)\beta(2) + \beta(1)\alpha(2)]$$

$$\frac{1}{2} [1s(1)2s(2) + 2s(1)1s(2)] \cdot \frac{1}{\sqrt{2}} [1s(1)2s(2) - 2s(1)1s(2)] [\alpha(1)\alpha(2)]$$

$$[\alpha(1)\beta(2) - \beta(1)\alpha(2)] \frac{1}{\sqrt{2}} [1s(1)2s(2) - 2s(1)1s(2)] [\beta(1)\beta(2)]$$

Anti-symmetric combination: “Singlet”

Symmetric combinations: “Triplet”

Pauli Principle Applied to 3 Electron Systems (Li)

Naively, we might expect the ground state of Li to be

$$1s(1)1s(2)1s(3)$$

- Of course, we know from introductory chemistry that this is not the case.
- The reason is that it is not possible to satisfy the Pauli principle for such a wavefunction.
- Since the orbital portion of the wavefunction is symmetric with respect to exchange of any 2 electrons, we would have to find a spin function that is antisymmetric with respect to exchange of all pairs.
- This is not possible!
- More generally, Pauli principle implies that 2 electrons that occupy the same orbital must have different spins, i.e.,

$$\psi = \psi_A(1)\psi_A(2)\alpha(1)\alpha(2)$$

[A and B are indices for 2 different orbitals.]

$$\hat{P}_{12}\psi = \psi$$

Violation of Pauli principle!

$$\psi = \psi_A(1)\psi_A(2)[\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

$$\psi = [\psi_A(1)\psi_B(2) - \psi_B(1)\psi_A(2)]\alpha(1)\alpha(2)$$

But these are just fine

Pauli Principle Symmetrization for Any Number of Electrons

Note that we can write, e.g., the ground state He atom wavefunction

$$\psi = 1s(1)1s(2)\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

as a determinant

$$\psi = \frac{1}{\sqrt{2}} \begin{vmatrix} 1s(1)\alpha(1) & 1s(1)\beta(1) \\ 1s(2)\alpha(2) & 1s(2)\beta(2) \end{vmatrix}$$

This is suggestive. In fact, any anti-symmetric wavefunction (with respect to permutation of any pair of electrons) can be written as

$$\psi = \frac{1}{\sqrt{n!}} \begin{vmatrix} f_1(1) & f_2(1) & f_3(1) & \cdots \\ f_1(2) & f_2(2) & f_3(2) & \cdots \\ f_1(3) & f_2(3) & f_3(3) & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{vmatrix}$$

*This is called
a “Slater
determinant”*

Why does this work? It's based on important, well-known properties of determinants:

1. Exchanging any 2 rows in a determinant multiplies it by -1.
[This is equivalent to "particle exchange".]
2. Exchanging any 2 columns in a determinant multiplies it by -1.
[This is equivalent to "orbital exchange".]
3. If 2 rows or 2 columns are identical, the determinant is zero.
[This is a way of stating that no 2 electrons may share the same orbital AND same spin.]

Now, all of a sudden it's easy to write out the properly symmetrized ground state wavefunction for Li:

$$\psi = \frac{1}{\sqrt{6}} \begin{vmatrix} 1s(1)\alpha(1) & 1s(1)\beta(1) & 2s(1)\alpha(1) \\ 1s(2)\alpha(2) & 1s(2)\beta(2) & 2s(2)\alpha(2) \\ 1s(2)\alpha(3) & 1s(3)\beta(3) & 2s(3)\alpha(3) \end{vmatrix}$$

A compact notation for writing this Slater determinant is

$$\psi = \left| 1s \bar{1}s \ 2s \right|$$

General multi-electron atomic Hamiltonian

$$\hat{H}_e^{eff}(\vec{r}_\alpha) = -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 - e^2 \sum_i \frac{Z}{r_i} + e^2 \sum_i \sum_{j>i} \left(\frac{1}{r_{ij}} \right)$$

nuclear charge

Key new term, relative to H atom: inter-electron repulsion; leads to “shielding” effects, splitting of s/p/d/f orbitals for same value of n, etc.

Atomic Units

Most electronic structure calculations are performed using an extremely convenient set of units called “atomic units”, in which both Planck’s constant and the electron mass and charge have values of exactly 1:

Mass: $m_e = 1$ (mass of electron)

Charge: $e = 1$ (charge of electron)

Angular momentum: $\hbar = 1$ (Planck’s constant)

Length: units of “Bohr” (0.53 Å; radius of classical H atom)

Energy: units of Hartree (4.36×10^{-18} J; potential energy of classical H atom)

Time: I don’t know what the units are called (2.42×10^{-17} s)

Speed of light: 137

In these units, the Hamiltonian simplifies nicely, e.g., for multielectron atoms:

$$\hat{H}_e^{eff}(\vec{r}_\alpha) = -\frac{1}{2} \sum_i \nabla_i^2 - \sum_i \frac{Z}{r_i} + \sum_i \sum_{j>i} \frac{1}{r_{ij}}$$

He

$$\begin{aligned}\hat{H}_e^{eff} &= -\frac{1}{2}\nabla_1^2 - \frac{1}{r_1} - \frac{1}{2}\nabla_2^2 - \frac{1}{r_2} + \frac{1}{r_{12}} \\ &= \hat{h}_1 + \hat{h}_2 + \frac{1}{r_{12}}\end{aligned}$$

Perturbation theory treatment of ground state: Use $1s(1)1s(2)$ wavefunction as the zero-order solution to be “perturbed” by the electron-electron repulsion.

$$E = E^\circ + \Delta E$$

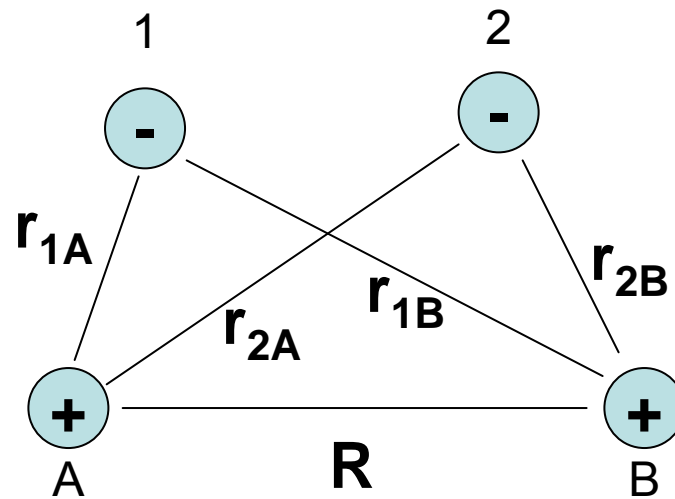
$$\Delta E = \int 1s(1)1s(2) \frac{1}{r_{12}} 1s(1)1s(2) = \frac{5Z}{8}$$

$$E^\circ = \frac{-Z^2}{2n^2} + \frac{-Z^2}{2n^2} = -Z^2$$

$$E = -4 + 1.25 = -2.75$$

*Experimental
value is -2.9037.*

H_2



In atomic units, and invoking the Born-Oppenheimer principle, the Hamiltonian is

$$\hat{H}_e^{eff}(\vec{r}_\alpha) = -\frac{1}{2}(\nabla_1^2 + \nabla_2^2) - \frac{1}{r_{1A}} - \frac{1}{r_{1B}} - \frac{1}{r_{2A}} - \frac{1}{r_{2B}} + \frac{1}{r_{12}} \left[+ \frac{1}{R} \right]$$

H₂ Valence Bond Treatment

It is possible to go through a very similar variational treatment as we applied previously for H₂⁺. I'm not going to go through it in detail. One key difference is that we have to deal with electron indistinguishability and the Pauli principle. But the really key difference is the electron-electron repulsion.

The basic strategy is to partition the Hamiltonian into a “zero-order part” and the “perturbation”. There are 2 equivalent ways to do this in the valence bond approach:

$$\hat{H}_e^{eff}(\vec{r}_\alpha) = \left(-\frac{1}{2} \nabla_1^2 - \frac{1}{r_{1A}} \right) + \left(-\frac{1}{2} \nabla_2^2 - \frac{1}{r_{2B}} \right) - \frac{1}{r_{1B}} - \frac{1}{r_{2A}} + \frac{1}{r_{12}}$$

$$= \hat{h}_{1A} + \hat{h}_{2B} - \frac{1}{r_{1B}} - \frac{1}{r_{2A}} + \frac{1}{r_{12}}$$

Coupling terms

**H-atom Hamiltonian for
electron 1 interacting
with nucleus A**

**H-atom Hamiltonian for
electron 2 interacting
with nucleus B**

Or equivalently ...

$$\hat{H}_e^{eff}(\vec{r}_\alpha) = \left(-\frac{1}{2} \nabla_1^2 - \frac{1}{r_{1B}} \right) + \left(-\frac{1}{2} \nabla_2^2 - \frac{1}{r_{2A}} \right) - \frac{1}{r_{1A}} - \frac{1}{r_{2B}} + \frac{1}{r_{12}}$$

$$= \hat{h}_{1B} + \hat{h}_{2A} - \frac{1}{r_{1A}} - \frac{1}{r_{2B}} + \frac{1}{r_{12}}$$

Coupling terms

**H-atom Hamiltonian for
electron 1 interacting
with nucleus B**

**H-atom Hamiltonian for
electron 2 interacting
with nucleus A**

Using a basis set of H-atom orbitals on each atomic center, we wind up with integrals in the “secular determinant” that are very similar to the coulomb, exchange, and overlap integrals that we derived for H_2^+ , except that now they involve 2 electrons, which makes them more complicated.

[It turns out that all the spin stuff basically “drops out” in the end; it’s more important for 3 and more electrons. So the integrals involve only spatial (orbital) integration.]

$$\begin{vmatrix} -1 - 2J' + J - E & -S^2 - 2SK' + K - ES^2 \\ -S^2 - 2SK' + K - ES^2 & -1 - 2J' + J - E \end{vmatrix} = 0$$

$$E = -1 + \frac{(J - 2J') \pm (K - 2SK')}{1 \pm S^2}$$

$$J' = \int 1s_A(1) \frac{1}{r_{1B}} 1s_A(1)$$

$$K' = \int 1s_A(1) \frac{1}{r_{1B}} 1s_B(1)$$

$$S = \int 1s_B(1) 1s_A(1)$$

These are identical to the integrals derived for H_2^+ , and are referred to as “1-center integrals” because they involve integration over the position of just one electron.

$$J = \iint 1s_A(1) 1s_B(2) \frac{1}{r_{12}} 1s_A(1) 1s_B(2)$$

$$K = \iint 1s_B(1) 1s_A(2) \frac{1}{r_{12}} 1s_A(1) 1s_B(2)$$

These are new relative to H_2^+ and arise from electron-electron repulsion. They are 2-center integrals. [Can get up to 4-center integrals for larger systems.]

Although the eigenenergy expressions are much more complicated, the wavefunctions wind up looking virtually identical (again, symmetry of the Hamiltonian dictates this):

$$\psi_{\pm} = \frac{1}{\sqrt{2(1 \pm S^2)}} [1s_A(1)1s_B(2) \pm 1s_B(1)1s_A(2)]$$

To get a complete wavefunction, we have to add in the proper spin wavefunctions to satisfy the Pauli principle, and we wind up with a singlet ground state and a triplet excited state.

A number of improvements are possible to this “valence bond” treatment:

1. Use more sophisticated basis sets (as opposed to the simple H atom functions) that take into account electron screening of the nuclei (simple strategy: scale the charges on the nuclei down a bit).
2. Add in p-orbitals, etc. This is referred to in the literature as “Generalized Valence Bond”.
3. Add in ionic structures. [We’ll come back to this in a second.]

H₂ Molecular Orbital Treatment

The basic idea: Instead of going back to the “linear combination of atomic orbitals” basis sets that underlie the valence bond approach, why not use the results that we obtained for H₂⁺ (“molecular orbitals”) as the basis set for H₂. In other words, the basis would be

$$1\sigma_g(1)1\sigma_g(2)$$

or more precisely, a properly anti-symmetrized Slater determinant

$$\frac{1}{\sqrt{2}} \begin{vmatrix} 1\sigma_g(1)\alpha(1) & 1\sigma_g(1)\beta(1) \\ 1\sigma_g(2)\alpha(2) & 1\sigma_g(2)\beta(2) \end{vmatrix}$$

This time, we group terms in the Hamiltonian differently:

$$\hat{H}_e^{eff} = \left(-\frac{1}{2} \nabla_1^2 - \frac{1}{r_{1A}} - \frac{1}{r_{1B}} \right) + \left(-\frac{1}{2} \nabla_2^2 - \frac{1}{r_{2A}} - \frac{1}{r_{2B}} \right) + \frac{1}{r_{12}}$$

$$= \hat{h}_1 + \hat{h}_2 + \frac{1}{r_{12}} \quad \text{Coupling term}$$

**H₂⁺ Hamiltonian
for electron 1**

**H₂⁺ Hamiltonian
for electron 2**

The conceptual advantage is clear; we know the solutions of the zero-order single-electron Hamiltonians, and so we only need to work on the pesky electron-electron repulsion.

Still, we know that the molecular orbitals can be expressed simply in terms of simple atomic orbitals, as in the valence bond approach, so there must be some pretty deep connections between the 2 approaches. For example,

$$1\sigma_g = \frac{1}{\sqrt{2(1 \pm S)}} [1s_A \pm 1s_B]$$

So let's form a 2 electron molecular orbital (forgetting about spin for the moment):

$$1\sigma_g(1)1\sigma_g(2) \propto [1s_A(1) + 1s_B(1)][1s_A(2) + 1s_B(2)]$$

$$= 1s_A(1)1s_B(2) + 1s_B(1)1s_A(2) + 1s_A(1)1s_A(2) + 1s_B(1)1s_B(2)$$

**This is just the
valence bond
eigenfunction ...**

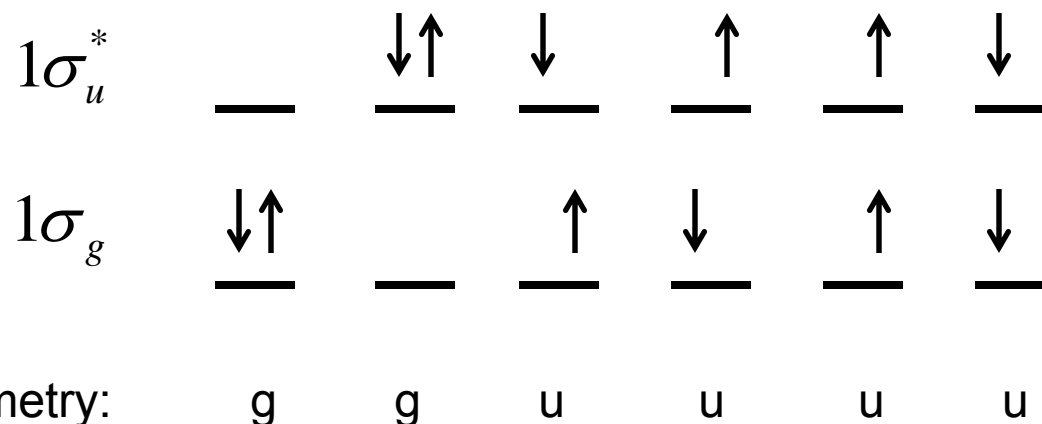
**... but we also
have these 2
extra terms.**

Physically, these “extra” terms correspond to placing both electrons on one atom, i.e., they represent ionic states: H^+H^- . There is a nice connection with Lewis dot structures:



- So the molecular orbital treatment includes ionic states, but valence bond does not.
- Does this mean that MO theory is better than VB?
- Yes and no. There is some probability of finding both electrons on the same atom, BUT the probability is relatively small (due to repulsion). In this “naive” MO approach, there is a 50/50 chance of finding the electrons on the same atom!
- VB approach is “fixed” by adding ionic states into the basis set.
- MO approach is “fixed” by adding in “configuration interaction” (include excited, anti-bonding states in the basis set) ...

But what excited states do we mix in??



The total Hamiltonian itself is symmetric with respect to inversion (i.e., “g”), so integrals of the type found in the secular determinant are zero, i.e.,

$$\int \sigma_g \hat{H} \sigma_u = 0$$

Thus, the first excited configuration that can mix with the ground state is

$$\begin{aligned} 1\sigma_u^*(1)1\sigma_u^*(2) &\propto [1s_A(1) - 1s_B(1)][1s_A(2) - 1s_B(2)] \\ &= 1s_A(1)1s_B(2) + 1s_B(1)1s_A(2) - 1s_A(1)1s_A(2) - 1s_B(1)1s_B(2) \end{aligned}$$

Note that the ionic and covalent basis functions come in with opposite signs from the ground state basis function, allowing them to be “decoupled”.

Conclusion of H₂ Investigation

Valence bond
+ ionic terms

=

Molecular orbital
+ configuration interaction

We've now reached the pinnacle of purity in this course. The variational principle allows highly accurate quantum eigenstates, but at a cost. Everything from here on in will be a series of increasingly drastic approximations, ranging from Hartree-Fock and DFT, to molecular mechanics with explicit and then implicit solvent, and finishing with docking. It's a long way down!