

Make sure you got these done from Tutorial 1 (important):

1. Variational methods are extremely important in quantum chemistry. They provide convenient and accurate numerical solutions to Schrödinger equations for many-electron systems for which analytical solutions do not exist.

To illustrate the **variational method**, use the trial function $\exp(-Ar)$ with A as a variational parameter to calculate the ground state energy of hydrogen-like atoms. Compare your answer with the exact result

$$E_n = -\frac{\mu e^4 Z^2}{8\epsilon_0^2 h^2 n^2}$$

The agreement is astonishingly good! Why?

2. Gaussian functions can be more convenient than exponential decays for numerical computer calculations involving integrals. For this reason, quantum chemistry computer software packages frequently use basis sets of Gaussian functions. Use the trial function $\exp(-Ar^2)$ with A as a variational parameter to calculate the ground state energy of hydrogen-like atoms. What is the magnitude of the error in the calculated energy?

New questions:

3. Why are Gaussian functions more convenient than Slater-type functions for numerical work? To illustrate the answer to this question, show that the product of a one-dimensional Gaussian function centered at x_A

$$\phi_A = \exp[-\alpha(x - x_A)^2]$$

and a one-dimensional Gaussian centered at x_B

$$\phi_B = \exp[-\beta(x - x_B)^2]$$

is a Gaussian centered at

$$x_p = \frac{\alpha x_A + \beta x_B}{\alpha + \beta}$$

This result can be generalized to the three-dimensional Gaussian functions used as basis sets to approximate molecular wave functions, allowing products of Gaussians to be efficiently integrated as a single Gaussian.

4. Crude solutions to Schrödinger equations for many-electron atoms systems are easily found by neglecting the mathematically complicated electron-electron repulsion terms. Unfortunately, the results are far from reality, mainly because the predicted atomic states are far too stable.

A much better and physically realistic approximation is to account for electron-electron repulsion by recognizing that the electrons screen each other from the nuclear charge Z , so each electron in a multi-electron atom "experiences" an effective nuclear charge $Z' < Z$. The concepts of screening and effective nuclear charge played a key role in Hartree-Fock calculations that gave the first explanation of the periodic table of elements.

The attached table provides Hartree-Fock values of Z'/n for electrons in atomic orbitals from helium to krypton. Illustrating the importance of nuclear screening, notice that the 3s electron in a sodium atom ($Z = 11$) "feels" an effective nuclear charge that is only $Z' = 3(0.8358) = 2.507$. The energy of a screened electron in a given orbital is estimated as $(Z')^2 E_{1s}/n^2$, where E_{1s} is the ground-state energy of the single-electron hydrogen atom (-13.60 eV).

← (see the last page)

a) Use the table of effective Z values to estimate the first ionization energy of Li atoms. (The experimental value is 5.32 eV.)

b) For the K and Ca atoms, which has the greater first ionization energy?

c) Does an electron in the 2s orbital of a K atom have a lower energy than the 1s electron in a hydrogen atom?

d) In photoelectron spectroscopy, high-energy X-rays or other radiation is used to eject electrons from orbitals, providing valuable information about the electronic structure of atoms and molecules. Estimate the wavelength of radiation required to eject an electron from the 2s orbital of a ground-state carbon atom.

5. Determine the term symbols for an np^1 electron configuration. Show that these term symbols are identical to those for an np^5 configuration. Which term symbol represents the ground state?

6. The term symbols for an nd^2 state are 1S , 1D , 3P , and 3F . Calculate the values of J associated with each of these term symbols. Which term represents the ground state?

7. An atom in a state with $L \neq 0$ and $S \neq 0$ produces a magnetic field (why?) and is said to be **paramagnetic**. Which of the first ten elements in the periodic table have paramagnetic ground states?

8. In the notes, the following term symbols are derived for the carbon electronic configuration $1s^2 2s^2 2p^2$

1D_2 3P_2 3P_1 3P_0 1S_0

Use Hund's rules to order these symbols in terms of increasing energy.

9. Once the allowed orbital and spin angular momentum states have been determined, the alignment of \vec{L} and \vec{S} to produce the total angular momentum \vec{J} can be computed.

Consider a 3D_2 state. In this example, $L = 2$, $S = 1$, and $J = 2$. The magnitudes of the orbital, spin, and total angular momentum vectors are

$$|\vec{L}| = \sqrt{L(L+1)} \hbar = \sqrt{6} \hbar$$

$$|\vec{S}| = \sqrt{S(S+1)} \hbar = \sqrt{2} \hbar$$

$$|\vec{J}| = \sqrt{J(J+1)} \hbar = \sqrt{6} \hbar$$

Vector addition of the angular and spin angular momentum gives the total angular momentum $\vec{J} = \vec{L} + \vec{S}$.

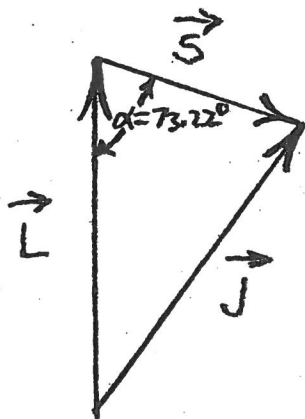
The geometric law of cosines

$$|\vec{J}|^2 = |\vec{L}|^2 + |\vec{S}|^2 - 2|\vec{L}||\vec{S}|\cos \alpha$$

can be used to calculate the angle between \vec{L} and \vec{S} . For the 3D_2 state, we obtain

$$6\hbar^2 = 6\hbar^2 + 2\hbar^2 - 2\sqrt{(6)(2)} \hbar^2 \cos \alpha$$

which gives $\cos \alpha = 1/\sqrt{12}$ and therefore $\alpha = 73.22$ degrees.



Give the corresponding vector diagrams and values of the angle α for the 1D_2 , 3P_2 , 3P_1 , 3P_0 , and 1S_0 terms derived in the notes for the $1s^2 2s^2 sp^2$ configuration of carbon and related [filled shell] np^2 configurations.

10. a) For $\alpha = 180^\circ$ (\vec{L} and \vec{S} pointing in the same direction), show that $J = L + S$.

b) For $\alpha = 0^\circ$ (\vec{L} and \vec{S} pointing in opposite directions), show that $J = |L - S|$.

Hence the useful rule that the range of possible values for quantum number J is $L + S, L + S - 1, L + S - 2, \dots, |L - S|$.

11. Electronic configurations with unpaired or paired spins have different energies, even though the Hamiltonian operator for the total energy contains no spin terms! In general, states with higher spin are lower in energy. This result has many important chemical consequences.

In the notes, it was mentioned, for example, that the triplet $1s^1 2s^1$ state of an excited helium atom has a lower energy than the singlet $1s^1 2s^1$ state. *Why?* Exact wave functions for helium atoms are unknown, but we can approximate them by using $1s$ and $2s$ single-electron wave functions. For the singlet wave function and energy, we have

$$\psi_{\text{singlet}} = \frac{1}{\sqrt{2}} [1s(1)2s(2) + 1s(2)2s(1)]$$

$$E_{\text{singlet}} = \frac{1}{2} \iint [1s(1)2s(2) + 1s(2)2s(1)] \left(\hat{H}_1 + \hat{H}_2 + \frac{e^2}{4\pi\epsilon_0 r_{12}} \right) [1s(1)2s(2) + 1s(2)2s(1)] d\tau_1 d\tau_2$$

a) Show that the two integrals containing \hat{H}_1 and \hat{H}_2 give the energies E_{1s} and E_{2s}

$$E_{1s} = -\frac{e^2}{2\pi\epsilon_0 a_0} \quad E_{2s} = -\frac{e^2}{8\pi\epsilon_0 a_0}$$

and therefore

$$E_{\text{singlet}} = E_{1s} + E_{2s} + \frac{1}{2} \iint [1s(1)2s(2) + 1s(2)2s(1)] \left(\frac{e^2}{4\pi\epsilon_0 r_{12}} \right) [1s(1)2s(2) + 1s(2)2s(1)] d\tau_1 d\tau_2$$

b) Show that the integral in the preceding equation for E_{singlet} can be rewritten as

$$\frac{1}{2} \iint [1s(1)2s(2) + 1s(2)2s(1)] \left(\frac{e^2}{4\pi\epsilon_0 r_{12}} \right) [1s(1)2s(2) + 1s(2)2s(1)] d\tau_1 d\tau_2 = J_{12} + K_{12}$$

J_{12} is the Coulomb integral for $1s$ and $2s$ electron-electron repulsion and K_{12} is the $1 \leftrightarrow 2$ "exchanged" integral

$$J_{12} = \frac{e^2}{8\pi\epsilon_0 r_{12}} \iint [1s(1)]^2 \left(\frac{1}{r_{12}} \right) [2s(2)]^2 d\tau_1 d\tau_2 \quad K_{12} = \frac{e^2}{8\pi\epsilon_0 r_{12}} \iint [1s(1)2s(2)] \left(\frac{1}{r_{12}} \right) [1s(2)2s(1)] d\tau_1 d\tau_2$$

which gives the singlet energy

$$E_{\text{singlet}} = E_{1s} + E_{2s} + J_{12} + K_{12}$$

c) Repeat this calculation for the triplet state with the antisymmetric wave function

$$\psi_{\text{triplet}} = \frac{1}{\sqrt{2}} [1s(1)2s(2) - 1s(2)2s(1)]$$

Show that the predicted triplet energy is $E_{\text{triplet}} = E_{1s} + E_{2s} + J_{12} - K_{12}$.

d) The predicted difference in energy between the triplet and singlet states is $E_{\text{triplet}} - E_{\text{singlet}} = -2K_{12}$. Show that K_{12} is positive, and so the triplet state is lower in energy. A detailed analysis shows that electron repulsion is slightly stronger for the triplet state, but the electrons are slightly closer to the nucleus, which gives the triplet state an overall energy that is lower than the singlet state. This important result can be generalized to show that a state with more unpaired spins has a lower energy than a corresponding state with fewer unpaired spins.

- ① } see notes from Tutorial #1
 ② }

$$\begin{aligned}
 \textcircled{3} \quad \int \phi_A(x) \phi_B(x) dx &= \int e^{-\alpha(x-x_A)^2} e^{-\beta(x-x_B)^2} dx \\
 &= \int e^{-\alpha(x-x_A)^2 - \beta(x-x_B)^2} dx = \int e^{-\alpha x^2 + 2\alpha x x_A - \alpha x_A^2 - \beta x^2 + 2\beta x x_B - \beta x_B^2} dx \\
 &= e^{-\alpha x_A^2} e^{-\beta x_B^2} \int e^{-\alpha x^2 + 2\alpha x x_A - \beta x^2 + 2\beta x x_B} dx \quad \text{factor out constants} \\
 &= e^{-(\alpha x_A^2 + \beta x_B^2)} \int e^{-(\alpha+\beta) \left[x^2 - 2x \frac{(\alpha x_A + \beta x_B)}{\alpha+\beta} \right]} dx \\
 &= e^{-(\alpha x_A^2 + \beta x_B^2)} \int e^{-(\alpha+\beta) \left[x^2 - 2x \frac{\alpha x_A + \beta x_B}{\alpha+\beta} + \left(\frac{\alpha x_A + \beta x_B}{\alpha+\beta} \right)^2 \right] + (\alpha+\beta) \left(\frac{\alpha x_A + \beta x_B}{\alpha+\beta} \right)^2} dx \\
 &= e^{-(\alpha x_A^2 + \beta x_B^2)} \int e^{-(\alpha+\beta) \left[x - \frac{\alpha x_A + \beta x_B}{\alpha+\beta} \right]^2} e^{(\alpha+\beta) \left(\frac{\alpha x_A + \beta x_B}{\alpha+\beta} \right)^2} dx \\
 &= e^{-(\alpha x_A^2 + \beta x_B^2)} \int e^{-(\alpha+\beta)(x-x_p)^2} e^{(\alpha+\beta)x_p^2} dx \quad \text{define } x_p = \frac{\alpha x_A + \beta x_B}{\alpha+\beta}
 \end{aligned}$$

$$= e^{(\alpha+\beta)x_p^2} e^{-(\alpha x_A^2 + \beta x_B^2)} \int e^{-(\alpha+\beta)(x-x_p)^2} dx$$

This is the integral of a single Gaussian centered on $x = x_p$

④ a) Li 2s electron $\frac{Z'}{n} = 0.6396$ (from appended table, $n=2$)

$$\text{electron energy} = \frac{(Z')^2}{n^2} E_{1s} = \frac{[2(0.6396)]^2}{2^2} (-13.60) \text{ eV} = -5.564 \text{ eV}$$

ionization energy = $+5.564 \text{ eV}$ (always positive)

(experiment: 5.32 eV $\approx 10\%$ lower)

(4 cont.)

.8738
.8738

b) K 4s electron $z'/4 = 0.8738$ $n=4$

$$\begin{aligned} \text{electron energy} &= \frac{(z')^2}{n^2} E_{1s} = \frac{[4(0.8738)]^2}{4^2} E_{1s} = 0.7635 E_{1s} \\ &= \boxed{-12.44 \text{ eV}} \end{aligned}$$

Ca 4s electron $z'/4 = 1.0995$

$$\begin{aligned} \text{electron energy} &= \frac{(z')^2}{n^2} E_{1s} = \frac{[4(1.0995)]^2}{4^2} E_{1s} = 1.2089 E_{1s} \\ &= \boxed{-16.44 \text{ eV}} \end{aligned}$$

Ca has the higher first ionization energy

(more stable)

c) 2s electron in K $z'/2 = 6.5031$

$$\text{electron energy} = \frac{(z')^2}{n^2} E_{1s} = \frac{[2(6.5031)]^2}{2^2} E_{1s} = \boxed{42.290 E_{1s}}$$

1s electron in H energy = $\boxed{E_{1s}}$

the 2s electron in K has an energy ≈ 42 times lower

d) ionization energy for a 2s electron in C

$$\left| \frac{(z')^2}{n^2} E_{1s} \right| = \frac{(2(1.6083))^2}{2^2} 13.60 \text{ eV} = \boxed{35.18 \text{ eV}}$$

$$h\nu = 35.18 \text{ eV} = \frac{hc}{\lambda}$$

$$\lambda = \frac{hc}{35.18 \text{ eV}}$$

$$\lambda = \frac{6.626 \times 10^{-34} (2.998 \times 10^8)}{35.18 (1.602 \times 10^{-19})} = \boxed{35.25 \text{ nm}} \quad (\text{an X-ray})$$

c) np^1 configuration $l=1$ $m = -1, 0, 1$

\uparrow = spin up (α) \downarrow = spin down (β)

np^1 six possibilities:

$m = 1$	\uparrow			\downarrow		
$m = 0$		\uparrow			\downarrow	
$m = -1$			\uparrow			\downarrow
M	1	0	-1	1	0	-1
M_S	$1/2$	$1/2$	$1/2$	$-1/2$	$-1/2$	$-1/2$
M_J	$3/2$	$1/2$	$-1/2$	$1/2$	$-1/2$	$-3/2$

The M and M_S values correspond to a 2P state.
 $M = 1, 0, -1 \Rightarrow L = 1$ $M_S = 1/2, -1/2 \Rightarrow S = 1/2$
 $\Rightarrow P$ term symbol with multiplicity $2S+1 = 2$

In general, values of J range from $L+S, L+S-1, \dots, |L-S|$.
 (never negative)

In this case $J = 1 + 1/2, 1 - 1/2$ or $3/2$ and $1/2$

$^2P_{3/2}$ or $^2P_{1/2}$ term symbols

the p -shell is less than half filled, so the $^2P_{1/2}$ state is the ground state.
 (Hund's 3rd rule)

$[Be]2p^1$ and $[Be]2p^5$ have the same term symbols because the single electron missing from the otherwise complete $[He]2p^5$ shell acts like a single electron "hole" or "vacancy" to be filled.

(5 cont.)

$m=1$	↓	↑↓	↑↓	↑	↑↓	↑↓
$m=0$	↑↓	↓	↑↓	↑↓	↑	↑↓
$m=-1$	↑↓	↑↓	↓	↑↓	↑↓	↑

M	1	0	-1	1	0	-1
M_S	1/2	1/2	1/2	-1/2	-1/2	-1/2
M_J	3/2	1/2	-1/2	1/2	-1/2	-3/2

(same as $2p^1$)

Similarly, the pairs np^2 and np^4 , nd^1 and nd^9 , nd^2 and nd^8 , etc. have identical term symbols

$$J = L+S, L+S-1, L+S-2, \dots, |L-S|$$

⑥ $nd^2 = {}^1S, {}^1D, {}^1G, {}^3P, {}^3F$

1S $S=0, L=0$ $J=0$ \Rightarrow 1S_0

1D $S=0, L=2$ $J=2$ \Rightarrow 1D_2

1G $S=0, L=4$ $J=4$ \Rightarrow 1G_4

3P $S=1, L=1$ $J=2, 1, 0$ ${}^3P_2, {}^3P_1, {}^3P_0$

3F $S=1, L=3$ $J=4, 3, 2$ ${}^3F_4, {}^3F_3, {}^3F_2$

According to Hund's first rule, the triplets ${}^3P_2, {}^3P_1, {}^3P_0, {}^3F_4, {}^3F_3, {}^3F_2$ have lower energies than the ${}^1S_0, {}^1D_2, {}^1G_4$ singlet states.

According to the second rule, the 3F states are lower in energy (larger L)

The nd^2 subshell is less than half full, so within the F states, the 3F_2 state (lowest J) has the lowest energy.

⑦ For an atom with $L \neq 0$ and $S \neq 0$, there is always orbital and/or spin electron angular momentum, and therefore a magnetic dipole.

Z			L	S	paramagnetic?
1	H	$2S_{1/2}$	0	1/2	
2	He	$1S_0$	0	0	
3	Li	$2S_{1/2}$	0	1/2	
4	Be	$1S_0$	0	0	
5	B	$2P_{1/2}$	1	1/2	yes
6	C	$3P_0$	1	1	yes
7	N	$4S_{3/2}$	0	3/2	
8	O	$3P_2$	1	1	yes
9	F	$3P_{3/2}$	1	1	yes
10	Ne	$1S_0$	0	0	

⑧ for the carbon $1s^2 2s^2 2p^2 = [Be] 2p^2$ configuration:

1D_2 3P_2 3P_1 3P_0 1S_0 possible states

Triplets have lower energies than singlets $^3P_2, ^3P_1, ^3P_0 < ^1D_2, ^1S_0$

the triplets are all P states, within the P states the states with lower J are more stable: $^3P_0 < ^3P_1 < ^3P_2$

within the singlets, the states with larger L are more stable
 $\therefore ^1D_2 < ^1S_0$

overall:
energies

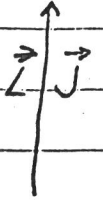
$$^3P_0 < ^3P_1 < ^3P_2 < ^1D_2 < ^1S_0$$

9) a) 1D_2 $L=2$ $S=0$ $J=2$

$$|\vec{L}| = \sqrt{2(3)} \hbar = \sqrt{6} \hbar$$

$$|\vec{S}| = 0$$

$$|\vec{J}| = \sqrt{2(3)} \hbar = \sqrt{6} \hbar$$



$$|\vec{J}|^2 = |\vec{L}|^2$$

$$\vec{J} = \vec{L}$$

$$\alpha = 180^\circ$$

b) 3P_2 $L=1$ $S=1$ $J=2$

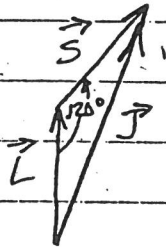
$$|\vec{L}| = \sqrt{2} \hbar$$

$$|\vec{S}| = \sqrt{2} \hbar$$

$$|\vec{J}| = \sqrt{6} \hbar$$

$$\cos \alpha = \frac{|\vec{J}|^2 - |\vec{L}|^2 - |\vec{S}|^2}{-2|\vec{L}||\vec{S}|} = \frac{6 - 2 - 2}{-2\sqrt{2}\sqrt{2}} = \frac{2}{-4} = -0.5$$

$$\alpha = 120^\circ$$



c) 3P_1 $L=1$ $S=1$ $J=1$

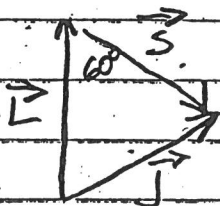
$$|\vec{L}| = \sqrt{2} \hbar$$

$$|\vec{S}| = \sqrt{2} \hbar$$

$$|\vec{J}| = \sqrt{2} \hbar$$

$$\cos \alpha = \frac{2 - 2 - 2}{-2\sqrt{2}\sqrt{2}} = \frac{2}{4} = 0.5$$

$$\alpha = 60^\circ$$



(9 cont.)

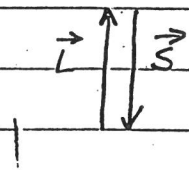
d) 3D_0 $L=1$ $S=1$ $J=0$
 $|\vec{L}| = \sqrt{2} \hbar$ $|\vec{S}| = \sqrt{2} \hbar$ $|\vec{J}| = 0$

$$|\vec{L}|^2 + |\vec{S}|^2 = 2|\vec{L}||\vec{S}| \cos \alpha$$

$$4 = 2\sqrt{2}\sqrt{2} \cos \alpha$$

$$\cos \alpha = 1$$

$$\alpha = 0^\circ$$



e) 1S_0 $L=0$ $S=0$ $J=0$
 $\vec{L}=0$ $\vec{S}=0$ $\vec{J}=0$

$$|\vec{J}|^2 = |\vec{L}|^2 + |\vec{S}|^2 - 2|\vec{L}||\vec{S}| \cos \alpha$$

(10) a) $\alpha = 180^\circ$ $\cos 180^\circ = -1$

$$|\vec{J}|^2 = |\vec{L}|^2 + |\vec{S}|^2 + 2|\vec{L}||\vec{S}|$$
$$= (|\vec{L}| + |\vec{S}|)^2$$

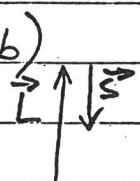
$$|\vec{J}| = \sqrt{(|\vec{L}| + |\vec{S}|)^2} = |\vec{L}| + |\vec{S}| = |\vec{L} + \vec{S}|$$



$$\sqrt{J(J+1)} \hbar = \sqrt{(L+S)(L+S+1)} \hbar$$

$$J = L+S$$

b) $\alpha = 0^\circ$ $\cos 0^\circ = 1$ $|\vec{J}|^2 = |\vec{L}|^2 + |\vec{S}|^2 - 2|\vec{L}||\vec{S}|$
 $= (|\vec{L}| - |\vec{S}|)^2$
 $= |\vec{L} - \vec{S}|^2$



$$\sqrt{J(J+1)} \hbar = \sqrt{(L-S)(L-S+1)} \hbar$$
$$J = |L-S|$$

$$E_{\text{singlet}} = \frac{1}{2} \iint \left[1s(1)2s(2) \pm 1s(2)2s(1) \right] \left(\hat{H}_1 + \hat{H}_2 + \frac{e^2}{4\pi\epsilon_0 r_{12}} \right) \left[1s(1)2s(2) \pm 1s(2)2s(1) \right] d\tau_1 d\tau_2$$

$$= \frac{1}{2} \iint \left[1s(1)2s(2) \pm 1s(2)2s(1) \right] \hat{H}_1 \left[1s(1)2s(2) \pm 1s(2)2s(1) \right] d\tau_1 d\tau_2$$

$$+ \frac{1}{2} \iint \left[1s(1)2s(2) \pm 1s(2)2s(1) \right] \hat{H}_2 \left[1s(1)2s(2) \pm 1s(2)2s(1) \right] d\tau_1 d\tau_2$$

$$+ \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \iint \left[1s(1)2s(2) \pm 1s(2)2s(1) \right] \frac{1}{r_{12}} \left[1s(1)2s(2) \pm 1s(2)2s(1) \right] d\tau_1 d\tau_2$$

recall: $\left. \begin{array}{ll} \hat{H}_1 1s(1) = E_{1s} & \hat{H}_1 1s(2) = 0 \\ \hat{H}_1 2s(1) = E_{2s} & \hat{H}_1 2s(2) = 0 \end{array} \right\}$ why? $\frac{\partial 1s(2)}{\partial r_1} = \frac{\partial 1s(2)}{\partial \theta_1} = \frac{\partial 1s(2)}{\partial \phi_1} = 0$

similarly, for electron 2:

$$\left. \begin{array}{ll} \hat{H}_2 1s(2) = E_{1s} & \hat{H}_2 1s(1) = 0 \\ \hat{H}_2 2s(2) = E_{2s} & \hat{H}_2 2s(1) = 0 \end{array} \right\}$$

$$\int 1s(1)1s(1) d\tau_1 = 1 = \int 1s(2)1s(2) d\tau_2$$

why?
orthonormal

$$\int 2s(1)2s(1) d\tau_1 = 1 = \int 2s(2)2s(2) d\tau_2$$

single-electron

wave functions

$$\int 1s(1)2s(1) d\tau_1 = \int 1s(2)2s(2) d\tau_2 = 0$$

$$E_{\text{singlet}} = \frac{1}{2} \iint \left[1s(1)2s(2) \pm 1s(2)2s(1) \right] \left[E_{1s} 1s(1)2s(2) \pm 1s(2)2s(1)E_{2s} \right] d\tau_1 d\tau_2$$

$$+ \frac{1}{2} \iint \left[1s(1)2s(2) \pm 1s(2)2s(1) \right] \left[E_{2s} 1s(1)2s(2) \pm E_{1s} 1s(2)2s(1) \right] d\tau_1 d\tau_2$$

$$+ \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \left[\iint \frac{[1s(1)2s(2)]^2}{r_{12}} d\tau_1 d\tau_2 + \iint \frac{[1s(2)2s(1)]^2}{r_{12}} d\tau_1 d\tau_2 \mp \iint \frac{1s(1)2s(2)1s(2)2s(1)}{r_{12}} d\tau_1 d\tau_2 \right]$$

11 cont.

$$E_{\text{singlet triplet}} = \frac{E_{1s}}{2} \iint 1s(1) 2s(2) 1s(1) 2s(2) d\tau_1 d\tau_2$$

$$+ \frac{E_{2s}}{2} \iint 1s(2) 2s(1) 1s(2) 2s(1) d\tau_1 d\tau_2$$

$$\pm \frac{E_{1s}}{2} \iint 1s(2) 2s(1) 1s(1) 2s(2) d\tau_1 d\tau_2$$

$$\pm \frac{E_{2s}}{2} \iint 1s(1) 2s(2) 1s(2) 2s(1) d\tau_1 d\tau_2$$

$$+ \frac{E_{2s}}{2} \iint 1s(1) 2s(2) 1s(1) 2s(2) d\tau_1 d\tau_2$$

$$+ \frac{E_{1s}}{2} \iint 1s(2) 2s(1) 1s(2) 2s(1) d\tau_1 d\tau_2$$

$$\pm \frac{E_{2s}}{2} \iint 1s(2) 2s(1) 1s(1) 2s(2) d\tau_1 d\tau_2$$

$$\pm \frac{E_{1s}}{2} \iint 1s(1) 2s(2) 1s(2) 2s(1) d\tau_1 d\tau_2$$

$$+ \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \left[\iint \frac{[1s(1) 2s(2)]^2}{r_{12}} d\tau_1 d\tau_2 + \iint \frac{[1s(1) 2s(2)]^2}{r_{12}} d\tau_1 d\tau_2 \right]$$

identical integrals
(electrons are indistinguishable)

$$\pm \frac{1}{2} \iint \frac{1s(1) 2s(2) 1s(2) 2s(1)}{r_{12}} d\tau_1 d\tau_2 \pm \iint \frac{1s(1) 2s(2) 1s(2) 2s(1)}{r_{12}} d\tau_1 d\tau_2$$

identical integrals ("")

11 cont.

$$E_{\text{singlet triplet}} = \frac{E_{1s}}{2} \int 1s(1)1s(1) d\tau_1 \int 2s(2)2s(2) d\tau_2$$

$$+ \frac{E_{2s}}{2} \int 2s(1)2s(1) d\tau_1 \int 1s(2)1s(2) d\tau_2$$

$$\pm \frac{E_{1s}}{2} \int 1s(1)2s(1) d\tau_1 \int 1s(2)2s(2) d\tau_2$$

$$\pm \frac{E_{2s}}{2} \int 1s(1)2s(1) d\tau_1 \int 1s(2)2s(2) d\tau_2$$

1s, 2s
wave
functions
are
orthonormal

$$+ \frac{E_{2s}}{2} \int 1s(1)1s(1) d\tau_1 \int 2s(2)2s(2) d\tau_2$$

$$+ \frac{E_{1s}}{2} \int 2s(1)2s(1) d\tau_1 \int 1s(2)1s(2) d\tau_2$$

$$\pm \frac{E_{2s}}{2} \int 2s(1)1s(1) d\tau_1 \int 1s(2)2s(2) d\tau_2$$

$$\pm \frac{E_{1s}}{2} \int 1s(1)2s(1) d\tau_1 \int 2s(2)1s(2) d\tau_2$$

$$+ \frac{e^2}{4\pi\epsilon_0} \iint \frac{[1s(1)2s(2)]^2}{r_{12}} d\tau_1 d\tau_2 \pm \frac{e^2}{4\pi\epsilon_0} \iint \frac{1s(1)2s(2)1s(2)2s(1)}{r_{12}} d\tau_1 d\tau_2$$

$\equiv J_{12}$ Coulomb integral $\equiv K_{12}$ Exchange Integral

$$E_{\text{singlet triplet}} = E_{1s} + E_{2s} + J_{12} \pm K_{12}$$

$$E_{\text{singlet}} - E_{\text{triplet}} = K_{12} - (-K_{12}) = 2K_{12}$$

K_{12} is positive (repulsion term) with $K_{12} = 1.19 \text{ eV}$

predict $E_{\text{singlet}} - E_{\text{triplet}} = 2.39 \text{ eV}$ (measure 0.80 eV)

Effective Values of Z'/n for Electrons in Atomic Orbitals

Atom	Z	1s	2s	2p	3s	3p	4s	3d	4p
He	2	1.6875							
Li	3	2.6906	0.6396						
Be	4	3.6848	0.9560						
B	5	4.6795	1.2881	1.2107					
C	6	5.6727	1.6083	1.5679					
N	7	6.6651	1.9237	1.9170					
O	8	7.6579	2.2458	2.2266					
F	9	8.6501	2.5638	2.5500					
Ne	10	9.6421	2.8792	2.8792					
Na	11	10.6259	3.2857	3.4009	0.8358				
Mg	12	11.6089	3.6960	3.9129	1.1025				
Al	13	12.5910	4.1068	4.4817	1.3724	1.3552			
Si	14	13.5745	4.5100	4.9725	1.6344	1.4284			
P	15	14.5578	4.9125	5.4806	1.8806	1.6288			
S	16	15.5409	5.3144	5.9885	2.1223	1.8273			
Cl	17	16.5239	5.7152	6.4966	2.3561	2.0387			
Ar	18	17.5075	6.1152	7.0041	2.5856	2.2547			
K	19	18.4895	6.5031	7.5136	2.8933	2.5752	0.8738		
Ca	20	19.4730	6.8882	8.0207	3.2005	2.8861	1.0995		
Sc	21	20.4566	7.2868	8.5273	3.4466	3.1354	1.1581	2.3733	
Ti	22	21.4409	7.6883	9.0324	3.6777	3.3679	1.2042	2.7138	
V	23	22.4256	8.0907	9.5364	3.9031	3.5950	1.2453	2.9943	
Cr	24	23.4138	8.4919	10.0376	4.1226	3.8220	1.2833	3.2522	
Mn	25	24.3957	8.8969	10.5420	4.3393	4.0364	1.3208	3.5094	
Fe	26	25.3810	9.2995	11.0444	4.5587	4.2593	1.3585	3.7266	
Co	27	26.3668	9.7025	11.5462	4.7741	4.4782	1.3941	3.9518	
Ni	28	27.3526	10.1063	12.0476	4.9870	4.6950	1.4277	4.1765	
Cu	29	28.3386	10.5099	12.5485	5.1981	4.9102	1.4606	4.4002	
Zn	30	29.3245	10.9140	13.0490	5.4064	5.1231	1.4913	4.6261	
Ga	31	30.3094	11.2995	13.5454	5.6654	5.4012	1.7667	5.0311	1.5554
Ge	32	31.2937	11.6824	14.0411	5.9299	5.6712	2.0109	5.4171	1.6951
As	33	32.2783	12.0635	14.5368	6.1985	5.9499	2.2360	5.7928	1.8623
Se	34	33.2622	12.4442	15.0326	6.4678	6.2350	2.4394	6.1590	2.0718
Br	35	34.2471	12.8217	15.5282	6.7395	6.5236	2.6382	6.5187	2.2570
Kr	36	35.2316	13.1990	16.0235	7.0109	6.8114	2.8289	6.8753	2.4423

Example For a 2s electron in Ne, $\frac{Z'}{n} = 2.8792$, $n=2$
 $Z' = 2.8792(2) = 5.7584$.