

Lecture 23: Many–Electron Atoms

Last Lecture:

- need to make a **small** approximation to pretend that the center of mass is at the nucleus, thus the coordinates are $\{\vec{r}_i\}$ for the electrons and $\vec{R} = 0$ for the nucleus
- For He, the inter–electron repulsion term

$$\frac{e^2}{|\vec{r}_1 - \vec{r}_2|} \quad \text{abbreviated as} \quad \frac{e^2}{r_{12}}$$

is bad news. It destroys n_1, ℓ_1, n_2, ℓ_2 orbital quantum numbers because it does not commute with $\hat{\ell}_1^2$ and $\hat{\ell}_2^2$.

- Non-interacting electron approximation: ignore $\frac{e^2}{r_{12}}$ term

$$E_{n_1, \ell_1; n_2, \ell_2} = -\frac{Z^2}{2n_1^2} - \frac{Z^2}{2n_2^2}.$$

Sum of H–atom orbital energies. The 2 in the denominator reflects our choice of atomic units where 1 au of Energy (the Hartree) is $2hc\mathcal{R}_\infty$.

- Independent electron approximation

$$\text{include} \quad \left\langle \frac{1}{r_{12}} \right\rangle$$

(like first-order perturbation theory).

- Electrons are identical, therefore wavefunctions must be eigenfunctions of permutation operator. All half-integer spin particles (where all e^- have $s = 1/2$) are Fermions, and the permutation symmetry for Fermions is

$$\hat{P}_{12}\Psi(1, 2) = \Psi(2, 1) = -\Psi(1, 2).$$

- Ψ is a product of a spatial and a spin part because $[\hat{\mathbf{H}}, \mathbf{S}^2] = 0$, and $[\hat{\mathbf{H}}, \mathbf{S}_Z] = 0$. The spin part of $\Psi(1, 2)$ must be an eigenfunction of $\hat{\mathbf{S}}^2$ and $\hat{\mathbf{S}}_z$. \mathbf{S} is the total electron spin. We know matrix elements of $\hat{\mathbf{S}}^2$, $\hat{\mathbf{S}}_x$, $\hat{\mathbf{S}}_y$, $\hat{\mathbf{S}}_z$, $\hat{\mathbf{S}}_+$ and $\hat{\mathbf{S}}_-$

$$\vec{\mathbf{S}} = \vec{\mathbf{s}}_1 + \vec{\mathbf{s}}_2.$$

For 2 electrons we have $S = 1$ (triplet) and $S = 0$ (singlet) spin eigenfunctions

		M_S
$S = 1$	$\alpha(1)\alpha(2)$	1
	$2^{-1/2}[\alpha(1)\beta(2) + \beta(1)\alpha(2)]$	0
	$\beta(1)\beta(2)$	-1
$S = 0$	$2^{-1/2}[\alpha(1)\beta(2) - \beta(1)\alpha(2)]$	0

The $S = 1$ eigenstates are SYMMETRIC. The $S = 0$ eigenstates are ANTI-SYMMETRIC.

- $\Psi(1, 2) = \Psi_{\text{space}}(\vec{r}_1, \vec{r}_2)\Psi_{\text{spin}}(\sigma_1, \sigma_2)$

Overall antisymmetry requirement is satisfied for

	space	spin	S
singlet	sym	anti	0
triplet	anti	sym	1

Even though \vec{S} makes no contribution to \hat{H} for Helium, the sym and anti *spatial* states have different energies. Thus, via permutation symmetry, spin makes an indirect but a large contribution to the eigen-energies and the form of the spatial eigenstates.

TODAY: MANY ELECTRON ATOMS

1. Slater determinants satisfy the general $P_{ij}\Psi(1, 2, \dots, i, \dots, j, \dots, n) = -\Psi$ anti-symmetrization requirement for all pairs of electrons.
2. Relationship between “stick diagrams” and Coulomb (\tilde{J}_{ij}) and Exchange (\tilde{K}_{ij}) integrals.
3. Qualitative Energetic Effects
 - a. Hund’s Rules
 - b. Shielding

Slater Determinants

For Helium $1s2s$

$$\Psi_{1s,2s}(1, 2) = 2^{-1/2} \underbrace{[1s(1)2s(2) \pm 2s(1)1s(2)]}_{\text{space}} 2^{-1/2} \underbrace{[\alpha(1)\beta(2) \mp \beta(1)\alpha(2)]}_{\text{spin}}$$

satisfies $\hat{P}_{12}\Psi(1, 2) = \Psi(2, 1) = -\Psi(1, 2)$.

How do we ensure, for $N > 2$ electrons, that

$$\hat{P}_{ij}\Psi(\dots i, j \dots) = -\Psi(\dots i, j \dots) \text{ for all } i, j?$$

Turns out that J. C. Slater [an MIT physicist, see *Phys. Review* **34**, 1293 (1929)] invented a very simple solution to this problem based on the properties of determinants.

Let us include all occupied “spin-orbitals”, which are a one-electron spatial orbital times either the α or β spin function, denoted as $\psi_{k_1}, \psi_{k_2}, \dots, \psi_{k_N}$. Then for N electrons we have Slater determinantal wavefunction

$$\Psi(1, 2, \dots, N) = [N!]^{-1/2} \begin{vmatrix} \psi_{k_1}(1) & \psi_{k_2}(1) & \dots & \psi_{k_N}(1) \\ \psi_{k_1}(2) & \psi_{k_2}(2) & \dots & \psi_{k_N}(2) \\ \dots & \dots & \dots & \dots \\ \psi_{k_1}(N) & \dots & \dots & \psi_{k_N}(N) \end{vmatrix}.$$

This bulky notation can be abbreviated to

$$[N!]^{-1/2} \begin{vmatrix} k_1(1) & \dots & k_N(1) \\ \dots & \dots & \dots \\ k_1(N) & \dots & k_N(N) \end{vmatrix}$$

or, better

$$[N!]^{-1/2} \begin{vmatrix} 1(1) & \dots & N(1) \\ \dots & \dots & \dots \\ 1(N) & \dots & N(N) \end{vmatrix}$$

or **BEST**

$$[N!]^{-1/2} |k_1 \quad \dots \quad k_2 \quad \dots \quad k_N|$$

which specifies only the main diagonal of the determinant.

Let's convince ourselves that these Slater determinants exhibit the properties we require using 2×2 determinants

$$\begin{aligned} & \begin{vmatrix} a & b \\ c & d \end{vmatrix} = ad - bc \\ \text{permute columns (electrons)} & \begin{vmatrix} b & a \\ d & c \end{vmatrix} = bc - ad \\ \text{permute rows (orbitals)} & \begin{vmatrix} c & d \\ a & b \end{vmatrix} = bc - ad \end{aligned}$$

So permutation of any two columns or rows causes a sign change in the value of the determinant.

Another wonderful property of determinants is that if any two columns or any two rows are the same, the value of the determinant is zero. Two identical columns would correspond to the two electrons in the same spin-orbital, which we know is illegal from the 5.111/5.112 “Pauli Exclusion Principle”.

$$\begin{vmatrix} a & a \\ c & c \end{vmatrix} = ac - ac = 0$$

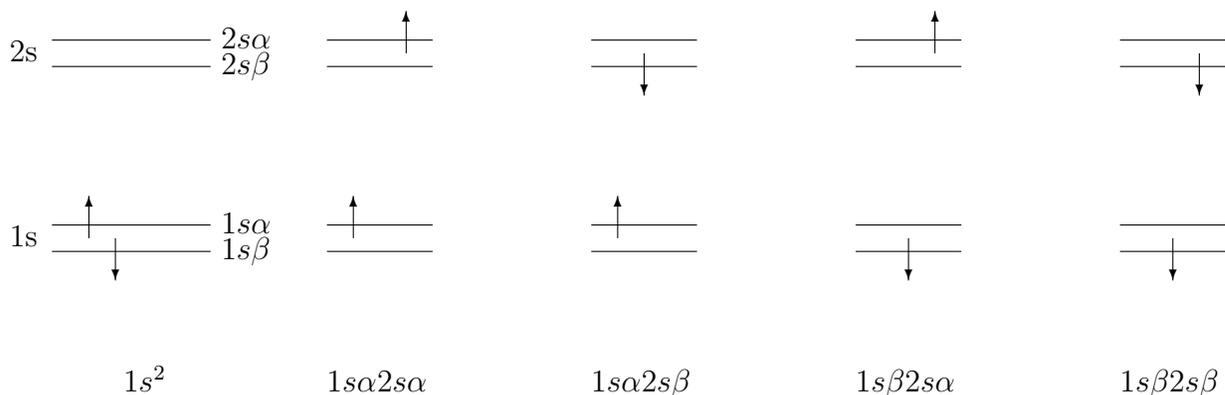
$$\begin{vmatrix} a & b \\ a & d \end{vmatrix} = ab - ab = 0.$$

It turns out that it is the anti-symmetry of Fermions that is the fundamental principle behind the convenient rule you memorized, perhaps even in High School. From the Pauli Exclusion Principle we get “*aufbau*”, which gives us some insight into the energy order of “configurations”: $n_1\ell_1 n_2\ell_2$, etc.

There is more to life than only the configuration, as we shall see.

Relationship between “stick diagrams” and Slater determinants.

Recall, for Helium, we used stick diagrams



(I have used the stick diagrams with an extra constraint, because I want to make the connection to spin-orbitals rather than simply to spatial orbitals.)

In the previous lecture we saw that, for 2-electron stick diagrams there was a direct relationship between each stick diagram and a pair of Coulomb (J_{ij}) and Exchange (K_{ij}) integrals. In the independent electron approximation, the expectation value of e^2/r_{12} , for two electrons

$$\langle \hat{\mathbf{H}}^{(1)} \rangle = \left\langle \Psi_{ij} \left| \frac{1}{r_{12}} \right| \Psi_{ij} \right\rangle = \tilde{J}_{ij} - \tilde{K}_{ij}.$$

The over-tilde’s warn us that we need to worry about the spin part of the integral.

Note that $1/r_{ij}$ does not depend on any spin coordinates. This means that all matrix elements of $1/r_{ij}$ must be diagonal in the spin (α/β) of the i and j electrons. For 2 electrons

$$\begin{aligned}\tilde{J}_{1s^2} &= J_{1s^2} & \tilde{K}_{1s^2} &= 0 \\ \tilde{J}_{1s\alpha,2s\alpha} &= J_{1s,2s} & \tilde{K}_{1s\alpha,2s\alpha} &= K_{1s,2s} \\ \tilde{J}_{1s\alpha,2s\beta} &= J_{1s,2s} & \tilde{K}_{1s\alpha,2s\beta} &= 0.\end{aligned}$$

If instead we look explicitly at the $\alpha\beta + \beta\alpha$ and $\alpha\beta - \beta\alpha$ spin eigen-states, we want

$$\left\langle 2^{-1/2}[\Psi_{1s\alpha,2s\beta} \pm \Psi_{1s\beta,2s\alpha}] \frac{1}{r_{12}} [\Psi_{1s\alpha,2s\beta} \pm \Psi_{1s\beta,2s\alpha}] \right\rangle$$

from which we get

$$\frac{1}{2}(J_{1s2s} + J_{1s2s}) \mp \frac{1}{2}(K_{1s2s} + K_{1s2s}) = J_{1s2s} \mp K_{1s2s}.$$

from diagonal terms
↑
from cross terms

↑
note that this sign reversal comes from the 1-2 electron permutation

Top sign corresponds to triplet

$$\begin{aligned}E_{3s} &= J_{1s,2s} - K_{1s,2s} \\ E_{1s} &= J_{1s,2s} + K_{1s,2s}\end{aligned}$$

as expected from previous lecture.

For the N -electron problem: use Slater determinants to compute energies. Some rules, that could be tediously derived ...

Non-Lecture

For a “one-electron” operator

- $\frac{-\nabla_i^2}{2} - \frac{Z}{r_i}$ (hydrogen atom)

- Zeeman effect

$$\hat{\mathbf{H}}^z = -B_Z(\mathbf{L}_z + 2\mathbf{S}_z) = -B_Z \sum_i (\ell_{zi} + 2s_{zi})$$

- Spin-Orbit

$$\hat{\mathbf{H}}^{\text{SO}} = a(r_i)\ell_i \cdot s_i = a(r_i) \left[\ell_{zi}s_{zi} + \frac{1}{2}(\ell_{+i}s_{-i} + \ell_{-i}s_{+i}) \right]$$

Selection Rule: $\Delta s_o = 0, 1$ (“so” refers to a spin-orbital)

For $\Delta s_o = 0$ (diagonal element)

$$\langle \Psi(N) | Op(i) | \Psi(N) \rangle = \sum_{i=1}^N \langle n_i \ell_i \sigma_i | Op(i) | n_i \ell_i \sigma_i \rangle$$

a sum of simple single-orbital integrals.

It is always the sum of all *diagonal* matrix elements between spin-orbitals.

For $\Delta s_0 = 1$

$$\langle \Psi(N) | Op(i) | \Psi'(N) \rangle = (-1)^p \langle n_i \ell_i \sigma_i | Op | n'_i \ell'_i \sigma'_i \rangle.$$

The $(-1)^p$ factor expresses the number of adjacent spin-orbital pair permutations needed to bring the mis-matched orbitals into the same location. For example:

$$\begin{aligned} \langle |abcd| Op(i) | acde \rangle & \quad b, e \text{ mis-match} \\ |acde| \rightarrow |aced| \rightarrow |aecd| & \quad p = 2 \end{aligned}$$

For a 2-electron operator, $Op(i, j)$, things are much more complicated and mostly beyond the scope of 5.61.

Selection rule: $\Delta s_0 = 0, 1, 2$.

End of Non-Lecture

Here we will consider only $\Delta S = 0$ for $Op(i, j) = \frac{e^2}{r_{ij}}$

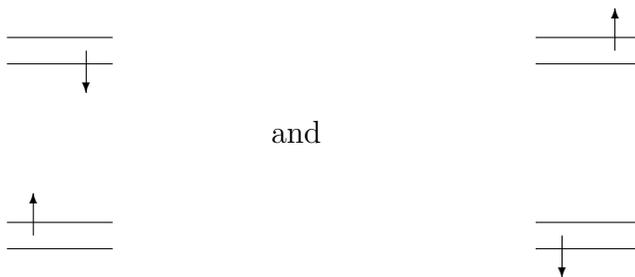
$$\langle \Psi(N) | Op(i, j) | \Psi(N) \rangle = \sum_{i=1}^N \sum_{j>i} (\tilde{J}_{ij} - \tilde{K}_{ij}).$$

The sum of orbital integrals extends over all pairs of spin-orbitals. Note that if $Op(i, j)$ does not depend on spin, the spin selection rule gives $\tilde{J}_{ij} = J_{ij}$ but $\tilde{K}_{ij} = 0$ if $\sigma_i \neq \sigma_j$ and $\tilde{K}_{ij} = K_{ij}$ if $\sigma_i = \sigma_j$.

There is an additional special case, where $\Psi(N)$ cannot be expressed as a single Slater determinant.

For example, consider the $M_S = 0$ states of the $1s2s$ configuration of Helium.

The stick diagrams



and



$1s\alpha 2s\beta$

$1s\beta 2s\alpha$

are needed to describe the $M_S = 0$ $S = 1$ and $M_S = 0$ $S = 0$ states. It is necessary to describe the 2-electron wavefunction $\Psi(2)$ by two Slater determinants

$$\Psi_{S,T}(2) = 2^{-1/2} [|1s\alpha, 2s\beta\rangle \pm |1s\beta, 2s\alpha\rangle].$$

There are four non-zero matrix elements:

$$\begin{aligned} \left\langle |1s\alpha, 2s\beta| \frac{1}{r_{12}} |1s\alpha, 2s\beta| \right\rangle &= J_{1s2s} \\ \left\langle |1s\alpha, 2s\beta| \frac{1}{r_{12}} |1s\beta, 2s\alpha| \right\rangle &= -K_{1s2s} \\ \left\langle |1s\beta, 2s\alpha| \frac{1}{r_{12}} |1s\alpha, 2s\beta| \right\rangle &= -K_{1s2s} \\ \left\langle |1s\beta, 2s\alpha| \frac{1}{r_{12}} |1s\beta, 2s\alpha| \right\rangle &= J_{1s2s}. \end{aligned}$$

Thus the overall $1/r_{12}$ matrix element for $\Psi_{S,T}(2)$ states with definite $\widehat{\mathbf{S}}^2$ character is

$$\left\langle \Psi(2) \left| \frac{1}{r_{12}} \right| \Psi(2) \right\rangle = \frac{1}{2} [2J_{1s2s} \mp 2K_{1s2s}]$$

top sign is $S = 1$ (triplet), bottom is $S = 0$ (singlet).

It is important to notice that both $|1s\alpha, 2s\beta|$ and $|1s\beta, 2s\alpha|$ are anti-symmetric with respect to electron permutation. Thus *both* of the $M_S = 0, S = 1$ and $M_S = 0, S = 0$ linear combinations of Slater determinants are also anti-symmetric.

$$\begin{aligned} P_{12}\Psi_{S,T}(2) &= 2^{-1/2} [|2s\beta, 1s\alpha| \pm |2s\alpha, 1s\beta|] \\ &= -2^{-1/2} [|1s\alpha, 2s\beta| \pm |1s\beta, 2s\alpha|] \\ &= -\Psi_{S,T}(2) \end{aligned}$$

Non-Lecture

Construction of eigenstates of $\widehat{\mathbf{S}}^2, \widehat{\mathbf{S}}_z, \widehat{\mathbf{L}}^2, \widehat{\mathbf{L}}_z$.

$\widehat{\mathbf{S}}$ is a vector sum of \widehat{s}_i .

$$\begin{aligned} \text{For two } e^-, \quad S &= 0 \text{ and } 1 \\ \text{For three } e^-, \quad S &= 3/2, 1/2, \text{ and } 1/2 \\ \text{For four } e^-, \quad S &= 2, 1, 1, 1, 0, 0 \end{aligned}$$

The eigenfunctions of $\widehat{\mathbf{S}}^2$ are tabulated in many publications (see page 151 of H. Lefebvre-Brion and R.W. Field, "Spectra and Dynamics of Diatomic Molecules", Elsevier, 2004).

Similarly for $\widehat{\mathbf{L}}$ as a sum of $\widehat{\ell}_i$.

Thus it is often necessary to evaluate J and K integrals for specific linear combinations of Slater determinants.

But here is an important simplification: since $\widehat{\mathbf{S}}^2, \widehat{\mathbf{S}}_z, \widehat{\mathbf{L}}^2,$ and $\widehat{\mathbf{L}}_z$ commute with $\widehat{\mathbf{H}}$ and the energies of the many-electron eigenstates of $\widehat{\mathbf{L}}^2$ and $\widehat{\mathbf{S}}^2$ do not depend on M_L and M_S , all you need to do is to find extreme M_L, M_S states: $M_L = L, M_S = S$ for maximum L for each S . These are *always* single Slater determinants.

Once you have done this, you could generate all $2L + 1$ M_L components and $2S + 1$ M_S components of these extreme L, S states by applying $\widehat{\mathbf{S}}_-$ and $\widehat{\mathbf{L}}_-$ lowering operators repeatedly.

The sum of the energies of all Slater determinants that are associated with a particular M_L, M_S block of $\hat{\mathbf{H}}$ is equal to the sum of the energies of all $\mathbf{L}^2, \mathbf{S}^2$ eigenstates represented in that block. This “trace invariance” provides a nice shortcut to determining *all* of the $E_{L,S}$ energies for each electronic configuration of a many electron atom.

End of Non-Lecture

3. Qualitative Energetic Effects

A. Hund's Rules

Hund's rules tell us which single $L - S - J$ eigenstate is expected to be the lowest energy eigenstate among *all* of the eigenstates that belong to a single electronic configuration.

For example, $1s2s$ gives 1S and 3S states. 3S is the lowest.

Another example, $2p3p$ gives $^3D, ^1D, ^3P, ^1P, ^3S,$ and 1S $L - S$ states. Each $L - S$ state has $J = L + S, L + S - 1, \dots, |L - S|$ total angular momentum J states. Of these $^3D_{J=1}$ is lowest.

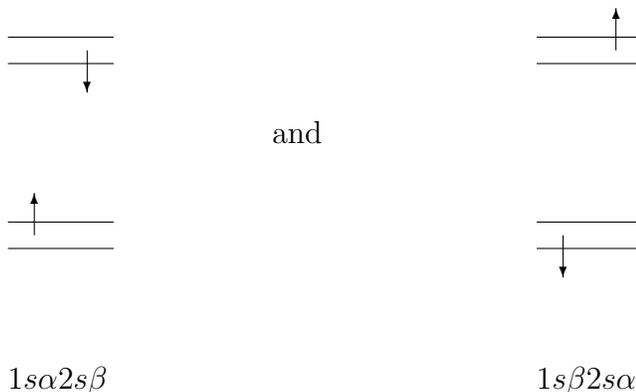
Hund's first rule: The lowest energy state is one where the S has maximum value.

Hund's second rule: The lowest energy state is, among those with maximum S , the one with maximum L .

Hund's third (and final) rule: The lowest energy J component of the single maximum- S , maximum- L state is $J = |L - S|$ if the ℓ -shell is less than half full (full shell for s is 2, p is 6, d is 10) and $J = L + S$ if the ℓ -shell is more than half-full.

Now I want to give you a tiny hint about where the first rule comes from.

Look again at the two $M_S = 0$ stick diagrams and the associated $S = 1$ (triplet) and $S = 0$ (singlet) states of $1s2s$.



$$\Psi(1, 2) = 2^{-1/2}[1s(1)2s(2) \pm 2s(1)1s(2)]2^{-1/2}[\alpha(1)\beta(2) \mp \beta(1)\alpha(2)]$$

top sign is singlet $S = 0, M_S = 0$

bottom sign is triplet $S = 1, M_S = 0$

Why is singlet state in $1s2s$ always at higher energy than triplet state?

Why? Electrons repel! What could be the most repulsive arrangement imaginable?

Suppose we try to put both electrons at the same position: $\vec{r}_1 = \vec{r}_2$. If we look at this special region of the spatial part of the two-electron wavefunction, we see something important:

$$1s(r_1)2s(r_2 = r_1) \pm 2s(r_1)1s(r_2 = r_1)$$

$$\text{bottom sign (triplet)} \quad \psi(r_1, r_2 = r_1) = 0!$$

$$\text{top sign (singlet)} \quad \psi(r_1, r_2 = r_1) \neq 0!$$

and very strong repulsion results for the singlet state.

This is a very suggestive argument that 1S is less stable (lies at higher E) than 3S .

This is borne out by the J_{1s2s} , K_{1s2s} integrals

$$E(^1S) - E(^3S) = 2K_{1s2s}$$

K is a repulsion energy so it is always positive.

Finally: here is a suggestion for why $K_{1s2s} < J_{1s2s}$. Rearrange the factors in the definition of the J and K integrals.

$$J_{1s2s} = \iint 1s(r_1)1s(r_1) \frac{1}{r_{12}} 2s(r_2)2s(r_2) dr_1 dr_2$$

$$1s(r_1)1s(r_1) = \rho_{1s}(r_1) \quad \text{a probability distribution}$$

$$2s(r_2)2s(r_2) = \rho_{2s}(r_2) \quad \text{another probability distribution}$$

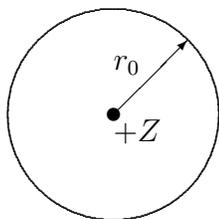
So J is the electrostatic interaction between two charge distributions. That is why we call it a *Coulomb integral*.

$$K_{1s2s} = \iint 1s(r_1)2s(r_1) \frac{1}{r_{12}} 1s(r_2)2s(r_2) dr_1 dr_2$$

$1s(r_1)2s(r_1)$ is not a probability distribution. It has complicated nodal structure, and it is less localized than either ρ_{1s} or ρ_{2s} . This means that $|K_{1s2s}| < |J_{1s2s}|$.

B. Shielding

In electrostatics, it is possible to calculate the Coulomb interaction between a point charge and a uniform spherical charge distribution.

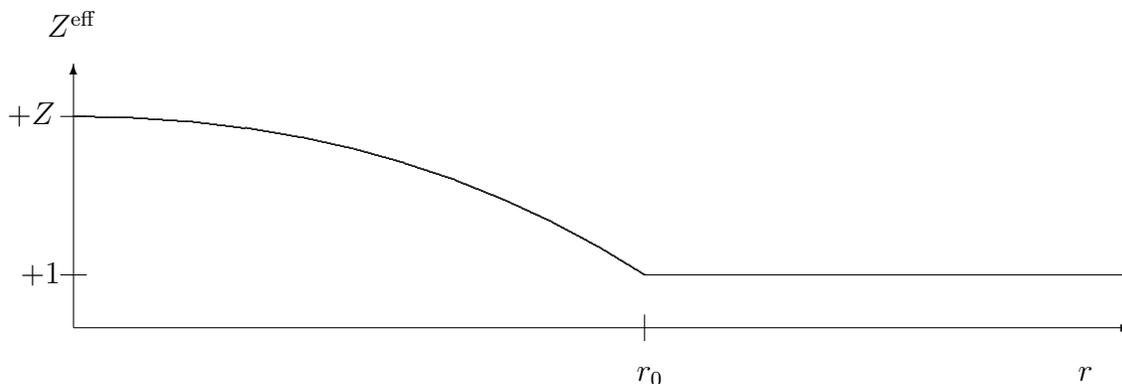


Suppose there is a $+Z$ point charge at the center of the uniform spherical charge distribution of radius r_0 . Suppose also that there are $Z - 1$ electrons in the charge distribution.

For the test charge at $r > r_0$, the test charge feels a Coulomb interaction equal to a charge of $+1$ at the center of the sphere.

For $r < r_0$, the test charge sees a larger effective charge. It sees an effective charge

$$Z_{\text{eff}} = Z - (Z - 1)(r/r_0)^3.$$



- e^- in inner orbitals shield nuclear charge from e^- in outer orbitals.
- All ns orbitals have amplitude at $r = 0$. This means that they feel a larger nuclear charge than all $\ell > 0$ orbitals because some ns amplitude “penetrates under” the e^- density in inner orbitals.
- The $\frac{\ell(\ell+1)}{r^2}$ centrifugal barrier keeps e^- in high- ℓ orbitals far outside the “ion-core”. High- ℓ orbitals see $Z_{\text{eff}} = +1$ (just like hydrogen).
- The shielding of the $+Z$ nuclear charge experienced by an electron in the $n'\ell'$ orbital is expressed by

$$\sum_{n\ell \neq n'\ell'} J_{n\ell, n'\ell'}.$$

This is a sum of repulsions of the $n\ell$ electron by the electron in the $n'\ell'$ orbital.

- We end up with a value of $Z_{n'\ell'}^{\text{eff}}$ that depends on which inner orbitals are filled and on the value of n' and ℓ' .

This explains why $E_{ns} < E_{np}$.

This also suggests why, as one goes from Ar $[1s^2, 2s^2, 2p^6, 3s^2, 3p^6]$ to K , the next electron goes into $4s$ rather than $3d$. And then Ca is $4s^2$ rather than $4s 3d$ or $3d^2$. But the big surprise is that even though $4s$ fills before $3d$, the electron that is easiest to remove from Sc $4s^2 3d$ and the other transition metals is $4s$ not $3d$. $3d$ shields the nucleus and causes $4s$ to become less stable because it sees a reduced Z^{eff} .

How do we improve on the Independent Electron Approximation?

One could imagine including something analogous to a second-order perturbation theory infinite summation. This can't work because, for many i, j

$$\left| \frac{H_{ij}^{(1)}}{E_i^{(0)} - E_j} \right| > 1,$$

which violates the convergence criterion of non-degenerate perturbation theory.

We could diagonalize a large $\hat{\mathbf{H}}$ matrix. The idea is somehow to build in some kind of $e^- - e^-$ correlation so that problems like regions of ψ where $r_1 = r_2$ are eliminated. There is a lot of magic in large dimension electronic structure calculations.

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