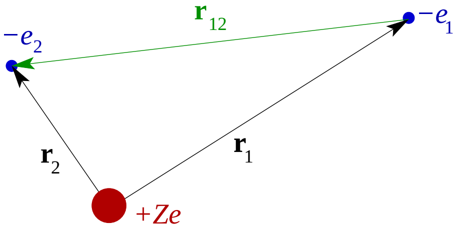
Helium and two electron atoms



Autumn 2013

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Coordinate system, Schrödinger Equation	3 slides
Evaluation of repulsion term	2 slides
Radial Integral - details	3 slides
Two electrons and spin	1 slide
Figures -helium spectra	3 slides
Symmetry and Antisymmetry of wavefunctions	2 slides in Para...
Parahelium and Orthohelium	4 slides + 1
Parahelium and Orthohelium in literature	1 slide + 1
Approximations to describe helium atom	3 slides
Helium atom - Exchange interaction	1 slide
Table - binding energies (or **with discussion**)	2+1 slides
Variational method and proof $\langle \phi \| H \| \phi \rangle \geq E_{g.s.}$	1 + 5 slides
Variational method with correlated function	1 slide
Configuration mixing	2 slides
Doubly excited states of Helium	3 slides + 4
Spin - Spin interaction - Ferromagnetism	2 slides
Atomic Units and formulae	optional

1 Description of Helium - 2 electron atom

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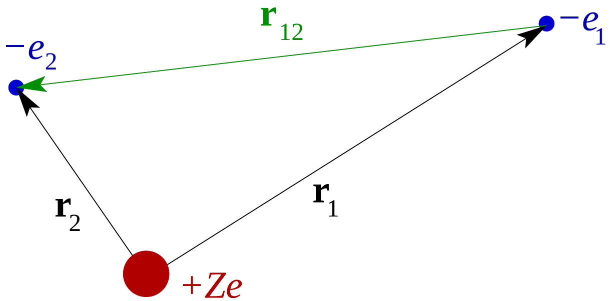
A helium atom consists of a nucleus of charge +2 surrounded by two electrons. The coordinates are shown in the drawing



The total energy is kinetic energy of the electrons (2 terms),

interaction of electrons with the nucleus (2 terms)

and the repulsion between the 2 electrons (1 term)

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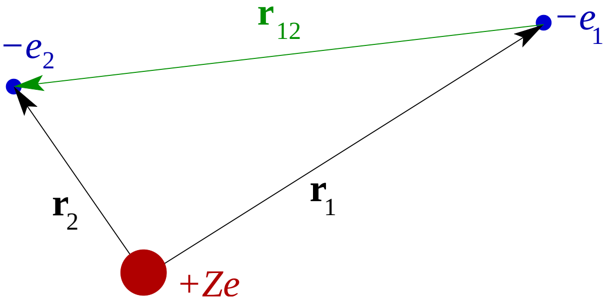
$$H = T_1(\mathbf{r}_1) \; + \; V_1(\mathbf{r}_1) \; + \; T_2(\mathbf{r}_2) \; + \; V_2(\mathbf{r}_2) \; + \; V_{12}(\mathbf{r}_1, \mathbf{r}_2)$$



$$\left[-\frac{\hbar^2}{2m_e} \nabla_{r_1}^{\,2} \; - \; \frac{Z\; e^2}{r_1} \; - \; \frac{\hbar^2}{2m_e} \nabla_{r_2}^{\,2} \; - \; \frac{Z\; e^2}{r_2} + \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \right] \Psi\left(\mathbf{r}_1, \mathbf{r}_2\right) \; = \; E\, \Psi\left(\mathbf{r}_1, \mathbf{r}_2\right)$$

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The wavefunction is a function of 6 variables, $\mathbf{r}_1$ and $\mathbf{r}_2$,
i.e. x_1, y_1, z_1, x_2, y_2, z_2.

$$\Psi\left(\mathbf{r}_1, \mathbf{r}_2\right)$$

The details of the operators:

$$H = T_1(\mathbf{r}_1) \ + \ V_1(\mathbf{r}_1) \ + \ T_2(\mathbf{r}_2) \ + \ V_2(\mathbf{r}_2) \ + \ V_{12}(\mathbf{r}_1, \mathbf{r}_2)$$

$$T_1(\mathbf{r}_1) \longrightarrow -\frac{\hbar^2}{2m_e}\nabla_{r_1}^{\,2} \qquad\qquad T_2(\mathbf{r}_2) \longrightarrow -\frac{\hbar^2}{2m_e}\nabla_{r_2}^{\,2}$$

$$V_1(\mathbf{r}_1) = -\frac{Z\ e^2}{|\mathbf{r}_1|} \quad \longrightarrow \quad -\frac{Z\ e^2}{r_1} \qquad\qquad V_2(\mathbf{r}_2) = -\frac{Z\ e^2}{r_2}$$

$$V_{12}(\mathbf{r}_1, \mathbf{r}_2) \ = \ +\frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \quad \longrightarrow \quad +\frac{e^2}{r_{12}}$$

Last term in the potential is repulsion between the electrons. Because of this term potential is not spherically symmetric in any two of the $\mathbf{r}_1$, $\mathbf{r}_2$.

There are 4 terms which work only on $\mathbf{r}_1$ or $\mathbf{r}_2$, but the repulsion term ”mixes” the two sets of variables

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2 Two electrons and spin

Spin is a new degree of freedom, discovered already in 1920's (W. Pauli)

Even if spin is not present in our Hamilton operator, it plays a very important role in the spectra.

Parahelium and **Orthohelium**

We will show:

Parahelium - singlet - includes the ground state

Orthohelium - triplet - excited states

(transitions "forbidden")

Addition of spin (or angular momentum):

$$\mathbf{S} = \mathbf{s}_1 + \mathbf{s}_2 \qquad \mathbf{L} = \mathbf{l}_1 + \mathbf{l}_2 \qquad \mathbf{J} = \mathbf{j}_1 + \mathbf{j}_2$$

$$J^2 = \mathbf{J} \cdot \mathbf{J} \qquad J^2 |j_1 j_2; JM\rangle = J(J+1) |j_1 j_2; JM\rangle \qquad |j_1 - j_2| \leq J \leq j_1 + j_2$$

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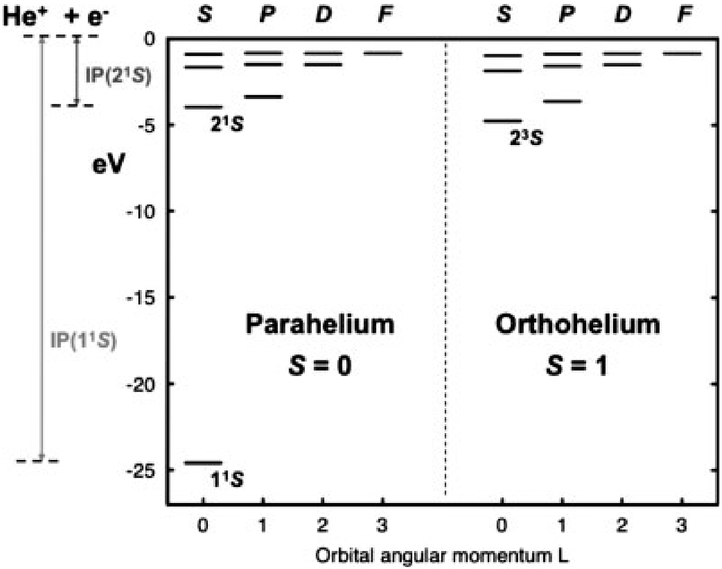

Figure 1:

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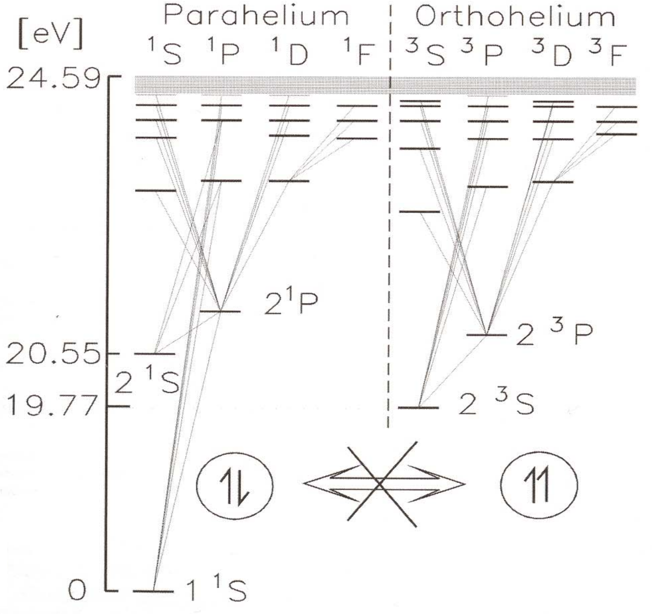

Figure 2: Para- and Ortho - Helium List of topics

Symmetry - Exclusion Principle Consider independent particles (product functions)

without symmetry (exclusion principle):

$$\Psi(1,2) = \phi_a(1)\phi_b(2) \tag{2}$$

Pauli principle:

$$\Psi(1,2) = [\ \phi_a(1)\phi_b(2) - \phi_b(1)\phi_a(2)\ ]\,/\sqrt{2}$$

Including ”spin variables” ξ_1, ξ_1,

$$\Psi(1,2) \ \longrightarrow\ \Psi(\mathbf{r}_1, \xi_1, \mathbf{r}_2, \xi_2)$$

Thus the total (independent) two particle wave function should be:

$$\Psi(\mathbf{r}_1, \xi_1, \mathbf{r}_2, \xi_2) = [\ \phi_a(\mathbf{r}_1)\chi_\alpha(\xi_1)\phi_b(\mathbf{r}_2)\chi_\beta(\xi_2) - \phi_b(\mathbf{r}_1)\chi_\beta(\xi_1)\phi_a(\mathbf{r}_2)\chi_\alpha(\xi_2)\ ]\,/\sqrt{2}$$

But this is not the case; since spin and space are independent, we must at the same time have

$$\Psi(1,2) = \ \Phi_{\text{space}}(1,2)\ \cdot\ \Xi_{\text{spin}}(1,2)$$

How to combine these two - make each antisymmetric? List of topics

The total function must be product of space and spin part and change sign on exchange $1 \longrightarrow 2$

$$\Psi(1,2) = \Phi^{\mathrm{Sym}}(\mathbf{r}_1, \mathbf{r}_2)\ \Xi^{\mathrm{Asym}}(\xi_1, \xi_2)$$

$$\Psi(1,2) = \Phi^{\mathrm{Asym}}(\mathbf{r}_1, \mathbf{r}_2)\ \Xi^{\mathrm{Sym}}(\xi_1, \xi_2)$$

This means in detail for the two types: symmetric space, antisymmetric spin

$$\left(\frac{1}{\sqrt{2}}[\ \phi_a(\mathbf{r}_1)\phi_b(\mathbf{r}_2) + \phi_b(\mathbf{r}_1)\phi_a(\mathbf{r}_2)]\right)\left(\frac{1}{\sqrt{2}}[\chi_\alpha(\xi_1)\chi_\beta(\xi_2) - \chi_\beta(\xi_1)\chi_\alpha(\xi_2)]\right)$$

or antisymmetric space, symmetric spin

$$\left(\frac{1}{\sqrt{2}}[\ \phi_a(\mathbf{r}_1)\phi_b(\mathbf{r}_2) - \phi_b(\mathbf{r}_1)\phi_a(\mathbf{r}_2)]\right)\left(\frac{1}{\sqrt{2}}[\chi_\alpha(\xi_1)\chi_\beta(\xi_2) + \chi_\beta(\xi_1)\chi_\alpha(\xi_2)]\right)$$

The mixed antisymmetric function mentioned first

$$\Psi(\mathbf{r}_1, \xi_1, \mathbf{r}_2, \xi_2) = [\ \phi_a(\mathbf{r}_1)\chi_\alpha(\xi_1)\phi_b(\mathbf{r}_2)\chi_\beta(\xi_2) - \phi_b(\mathbf{r}_1)\chi_\beta(\xi_1)\phi_a(\mathbf{r}_2)\chi_\alpha(\xi_2)\ ]/\sqrt{2}$$

describes space and spin coupled. That is *spin-orbit coupling* or *j-j coupling*; in heavy atoms, not in helium.

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There are four product combinations:
$\chi_\uparrow(\xi_1)\chi_\uparrow(\xi_2)$, $\chi_\downarrow(\xi_1)\chi_\downarrow(\xi_2)$, $\chi_\uparrow(\xi_1)\chi_\downarrow(\xi_2)$ and $\chi_\downarrow(\xi_1)\chi_\uparrow(\xi_2)$

They can be combined to three symmetric (triplet) and a single one antisymmetric (singlet)

$$\begin{aligned}
&\chi_\uparrow(\xi_1)\chi_\uparrow(\xi_2)\\
&\chi_\downarrow(\xi_1)\chi_\downarrow(\xi_2)\\
&\frac{1}{\sqrt{2}}\left[\chi_\uparrow(\xi_1)\chi_\downarrow(\xi_2)+\chi_\downarrow(\xi_1)\chi_\uparrow(\xi_2)\right]\\
&\frac{1}{\sqrt{2}}\left[\chi_\uparrow(\xi_1)\chi_\downarrow(\xi_2)-\chi_\downarrow(\xi_1)\chi_\uparrow(\xi_2)\right]
\end{aligned}$$

We can also use a more compact notation

$$\begin{aligned}
&\uparrow(1)\uparrow(2)\\
&\downarrow(1)\downarrow(2)\\
&\frac{1}{\sqrt{2}}\left[\uparrow(1)\downarrow(2)+\downarrow(1)\uparrow(2)\right]\\
&\frac{1}{\sqrt{2}}\left[\uparrow(1)\downarrow(2)-\downarrow(1)\uparrow(2)\right]
\end{aligned}$$

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3 Why are the Ortho-helium states lower in energy than the Para-helium states?

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The SPATIAL symmetric combination

$$\Psi_S(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} [\ \phi_a(\mathbf{r}_1)\phi_b(\mathbf{r}_2) + \phi_b(\mathbf{r}_1)\phi_a(\mathbf{r}_2)\ ] \qquad \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

when $\mathbf{r}_1 \to \mathbf{r}_2$

$$\Psi_S(\mathbf{r}, \mathbf{r}) \to \frac{1}{\sqrt{2}} [\ \phi_a(\mathbf{r})\phi_b(\mathbf{r}) + \phi_b(\mathbf{r})\phi_a(\mathbf{r})\ ] \to \sqrt{2}\phi_a(\mathbf{r})\phi_b(\mathbf{r}) \qquad S = 0$$

i.e. close to maximum. The the repulsion as large as possible, in the $S = 0$ singlet

The SPATIAL antisymmetric combination (spin must be thus symmetric; triplet)

$$\Psi_A(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} [\ \phi_a(\mathbf{r}_1)\phi_b(\mathbf{r}_2) - \phi_b(\mathbf{r}_1)\phi_a(\mathbf{r}_2)\ ]$$

when $\mathbf{r}_1 \to \mathbf{r}_2$

$$\Psi_A(\mathbf{r}, \mathbf{r}) \to \frac{1}{\sqrt{2}} [\ \phi_a(\mathbf{r})\phi_b(\mathbf{r}) - \phi_b(\mathbf{r})\phi_a(\mathbf{r})\ ] \to 0 \qquad S = 1$$

Repulsion term - exchange interaction

Singlet, $S = 0$, space symmetric — Repulsion large

Triplet, $S = 1$, space antisymmetric — Repulsion small

Can also be related to the sign of Exchange term

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4 Various formulations found in literature

The probability for small separations of the electrons is less for anti-symmetric than for symmetric space wave functions. (our formulation is better!)

If then the electrons are further apart on average, there will be less shielding of the nucleus by the ground state electron,and thus the excited state electron will be more exposed to the nucleus.

This implies that the ortho-helium states will be more tightly bound and of lower energy. (our formulation is much better and much more correct !)

Helium energy levels (singly excited)

1) np state spin anti-parallel to the spin of 1s state: S=0, singlet state, Para-helium

2) np state spin parallel to the spin of 1s state: S=1, triplet state, Ortho-helium

The $S = 0$ and $S = 1$ difference can also be related to the sign of Exchange term

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5 Spin - Spin interaction - Ferromagnetism

The triplet - singlet difference in energy acts as a result of an effective spin-spin interaction. When spins are parallel ($S = 1$) repulsion weaker - i.e. *effective attraction*

$$\mathbf{S} = \mathbf{s}_1 + \mathbf{s}_2 \qquad \mathbf{S}^2 = \mathbf{S} \cdot \mathbf{S} = (\mathbf{s}_1 + \mathbf{s}_2) \cdot (\mathbf{s}_1 + \mathbf{s}_2) = \mathbf{s}_1^2 + \mathbf{s}_2^2 + 2\ \mathbf{s}_1 \cdot \mathbf{s}_2$$

$$\langle S|\mathbf{S}^2|S\rangle = S(S+1) = \frac{3}{4} + \frac{3}{4} + 2\langle S|\mathbf{s}_1 \cdot \mathbf{s}_2|S\rangle \rightarrow \langle S|\mathbf{s}_1 \cdot \mathbf{s}_2|S\rangle = \frac{S(S+1)}{2} - \frac{3}{4}$$

We see then that for the triplet $|1\rangle$ and singlet $|0\rangle$

$$\langle 1|\mathbf{s}_1 \cdot \mathbf{s}_2|1\rangle = \frac{1}{4} \qquad \langle 0|\mathbf{s}_1 \cdot \mathbf{s}_2|0\rangle = -\frac{3}{4}$$

We now attempt to write the two energies $E(S)$ as function of $\langle S|\mathbf{s}_1 \cdot \mathbf{s}_2|S\rangle$

$$E(S) = A - B\ \langle S|\mathbf{s}_1 \cdot \mathbf{s}_2|S\rangle \qquad E(1) = A - B\frac{1}{4} \qquad E(0) = A + B\frac{3}{4}$$

It is easily seen that the energy constants A and B must be

$$A = \frac{3}{4}E(1) + \frac{1}{4}E(0) \qquad B = E(0) - E(1) \qquad (B > 0)$$

The energy difference E(0) - E (1) can be seen as a result of an effective interaction

$$V(\mathbf{s}_1, \mathbf{s}_2) = A - B\ (\mathbf{s}_1 \cdot \mathbf{s}_2)$$

As one would expect, $\mathbf{s}_1 \cdot \mathbf{s}_2$ is positive for triplets S=1, the spins are parallel, and negative for S=0 singlet, the spins are antiparallel, as we have seen above in

$$\langle 1|\mathbf{s}_1 \cdot \mathbf{s}_2|1\rangle = \frac{1}{4} \qquad\qquad \langle 0|\mathbf{s}_1 \cdot \mathbf{s}_2|0\rangle = -\frac{3}{4}$$

The energy difference is caused by the electrostatic repulsion term, being suppressed in the triplet (S=1) case due to the space-antisymmetry, or we can say Pauli principle.

The nature of ferromagnetism is such spin-spin interaction, i.e. the correlation of spins is caused by electrostatic (atomic) interactions (that is why it is so strong). This correlates the spin magnetic moments, so that a magnetised material has a magnetic moment.

The magnetic spin-spin interactions is much weaker and could not cause a permanent correlation.

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6 Approximations to describe helium atom

To obtain simplified solutions the Schrödinger we first disregard the repulsion term (and then treat the repulsion using approximations)

$$\left[-\frac{\hbar^2}{2m_e}\nabla_{r_1}^2 - \frac{Z\ e^2}{r_1} - \frac{\hbar^2}{2m_e}\nabla_{r_2}^2 - \frac{Z\ e^2}{r_2} + \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|}\right]\Psi(\mathbf{r}_1,\mathbf{r}_2) = E\ \Psi(\mathbf{r}_1,\mathbf{r}_2)$$

Independent electron approach ⟶ wave function is separable

$$\left[-\frac{\hbar^2}{2m_e}\nabla_{r_1}^2 - \frac{Z\ e^2}{r_1} - \frac{\hbar^2}{2m_e}\nabla_{r_2}^2 - \frac{Z\ e^2}{r_2}\right]\Psi_1(\mathbf{r}_1)\,\Psi_2(\mathbf{r}_2) = (E_1+E_2)\,\Psi_1(\mathbf{r}_1)\,\Psi_2(\mathbf{r}_2)$$

$$\left[-\frac{\hbar^2}{2m_e}\nabla_{r_1}^2 - \frac{Z\ e^2}{r_1}\right]\Psi_1(\mathbf{r}_1) = E_1\ \Psi_1(\mathbf{r}_1) \qquad \left[-\frac{\hbar^2}{2m_e}\nabla_{r_2}^2 - \frac{Z\ e^2}{r_2}\right]\Psi_2(\mathbf{r}_2) = E_2\ \Psi_2(\mathbf{r}_2)$$

Finally, the repulsion term can be included, - introducing various approximation methods (Perturbation theory, Variational method)

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The above two eqs. Are identical to Schrödinger eq. for H-atom - but where Nuclear charge is +Ze instead of +e

To obtain **simplest approximation** to the solutions of the Schrödinger we started by disregarding the repulsion term alltogether.

The above Schrödinger equation is now separable into two equations - each for one electron (Independent electron approach: wave function is separable)

The energy of the ground state (see the table)

$$E = E_{1s}(Z) + E_{1s}(Z) = 2Z^2\frac{1}{2}E_0$$

Next approximation: perturbation theory

Keep the same "Independent electron approach" wavefunctions, but evaluate **expectation value** of the repulsion integral

$$\left\langle \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \right\rangle_Z = \frac{5}{8}Z\ E_0 \quad (\ = 17\ eV\ \ for\ Z = 1\ )\ (\ = 34\ eV\ \ for\ Z = 2\ )$$

Next improvement of independent (separable) wavefunction: Variational method

Best results: functions including correlations; non-separable; not independent electrons

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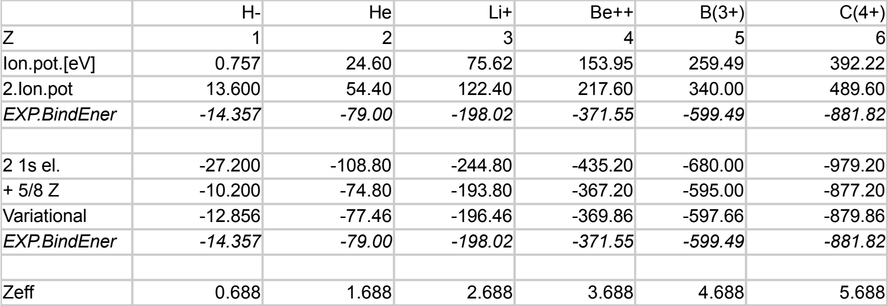

	H-	He	Li+	Be++	B(3+)	C(4+)
Z	1	2	3	4	5	6
Ion.pot.[eV]	0.757	24.60	75.62	153.95	259.49	392.22
2.Ion.pot	13.600	54.40	122.40	217.60	340.00	489.60
EXP.BindEner	*-14.357*	*-79.00*	*-198.02*	*-371.55*	*-599.49*	*-881.82*
2 1s el.	-27.200	-108.80	-244.80	-435.20	-680.00	-979.20
+ 5/8 Z	-10.200	-74.80	-193.80	-367.20	-595.00	-877.20
Variational	-12.856	-77.46	-196.46	-369.86	-597.66	-879.86
EXP.BindEner	*-14.357*	*-79.00*	*-198.02*	*-371.55*	*-599.49*	*-881.82*
Zeff	0.688	1.688	2.688	3.688	4.688	5.688

Figure 3: Table of approximation results (in electronVolts)

$$E_{1s}(Z=1) \;=\; -13.6eV \;=\; -0.5E_0$$

($E_0 \;=\; 27.2eV$ is the atomic unit of energy)

$$E_{1s}(Z) \;=\; -Z^2 13.6eV \;=\; -0.5Z^2\;\; E_0$$

$$\left\langle \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \right\rangle_Z = \frac{5}{8} Z\; E_0 \quad (\,=17\;eV\;\; for\;\; Z=1\;)\;(\,=34\;eV\;\; for\;\; Z=2\;)$$

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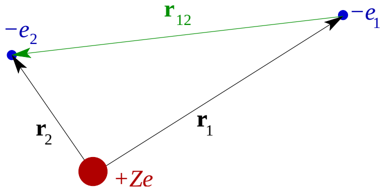

For general states in Helium

$$\left[-\frac{\hbar^2}{2m_e}\nabla^2_{r_1} - \frac{Z\ e^2}{r_1} - \frac{\hbar^2}{2m_e}\nabla^2_{r_2} - \frac{Z\ e^2}{r_2} + \frac{e^2}{|\mathbf{r}_1-\mathbf{r}_2|}\right]\Psi\left(\mathbf{r}_1,\mathbf{r}_2\right) = E\ \Psi\left(\mathbf{r}_1,\mathbf{r}_2\right)$$

$$\Phi^{HF}_{a,b}\left(r_1,r_2\right) = \frac{1}{\sqrt{2}}\left|\begin{array}{cc} \psi_a(r_1) & \psi_b(r_1) \\ \psi_a(r_2) & \psi_b(r_2) \end{array}\right| = \frac{1}{\sqrt{2}}\left[\psi_a(r_1)\psi_b(r_2)-\psi_b(r_1)\psi_a(r_2)\right]$$

and the energy becomes

$$\begin{aligned}\left\langle\Phi^{HF}\middle|H\middle|\Phi^{HF}\right\rangle &= \langle\psi_a|\,T-\frac{Ze^2}{r}\,|\psi_a\rangle + \langle\psi_b|\,T-\frac{Ze^2}{r}\,|\psi_b\rangle \\ &+ \langle\psi_a\psi_b|\,\frac{e^2}{|\mathbf{r}-\mathbf{r}'|}\,|\psi_a\ \psi_b\ \rangle - \langle\psi_a\psi_b|\,\frac{e^2}{|\mathbf{r}-\mathbf{r}'|}\,|\psi_b\ \psi_a\ \rangle \qquad (3)\end{aligned}$$

The last term - **exchange energy**. THIS APPLIES to TRIPLET STATES.
For SINGLET STATES - the exchange term sign is changed to +.

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7 Repulsion term - multipole expansion

$$\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} = \sum_{LM} \frac{4\pi}{2L+1} \, \frac{r_<^L}{r_>^{L+1}} \, Y_{LM}^{\star}\left(\hat{r}_1\right) Y_{LM}\left(\hat{r}_2\right) \tag{4}$$

where

$$r_< = r_1, \quad r_> = r_2 \quad \text{for} \quad |\mathbf{r}_1| \; < \; |\mathbf{r}_2|$$

$$r_< = r_2, \quad r_> = r_1 \quad \text{for} \quad |\mathbf{r}_1| \; > \; |\mathbf{r}_2|$$

Evaluation of the matrix element in general case

$$\int d^3\mathbf{r}_1 \int d^3\mathbf{r}_2 \psi_{n_1 l_1 m_1}^{\star}\left(\mathbf{r}_1\right) \psi_{n_2 l_2 m_2}^{\star}\left(\mathbf{r}_2\right) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \psi_{n_1 l_1 m_1}\left(\mathbf{r}_1\right) \psi_{n_2 l_2 m_2}\left(\mathbf{r}_2\right) \tag{5}$$

is performed separately over the radial and angular parts

$$\begin{aligned} \int r_1^2 dr_1 \int d\hat{r}_1 \int r_2^2 dr_2 \int d\hat{r}_2 \qquad & R_{n_1 l_1}^{\star}(r_1) Y_{l_1 m_1}^{\star}\left(\hat{r}_1\right) R_{n_2 l_2}^{\star}(r_2) Y_{l_2 m_2}^{\star}\left(\hat{r}_2\right) \\ \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \qquad & R_{n_1 l_1}(r_1) Y_{l_1 m_1}\left(\hat{r}_1\right) R_{n_2 l_2}(r_2) Y_{l_2 m_2}\left(\hat{r}_2\right) \end{aligned} \tag{6}$$

where $d\hat{r}_i$ means the integration over $d\Omega_i = \sin\theta_i d\theta_i d\varphi_i$.

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The evaluation of general case - angular integrals of three Y_{lm}'s

$$C^L = \int Y^\star_{l_i m_i}(\theta, \varphi) Y_{LM}(\theta, \varphi) Y_{l_i m_i}(\theta, \varphi) d\Omega \tag{7}$$

For the case of both s-states, $l_i = 0 \quad m_i = 0$ only $L = 0 \quad M = 0$ are non-zero; The sum reduces to one term. The angular factors give value one, since the $(Y_{L=0M=0})^2 = (4\pi)^{-1}$ cancels the corresponding factor in the multipole expansion and due to the normalization.

Thus the repulsion matrix element with the e^2 encluded

$$\int d^3\mathbf{r}_1 \int d^3\mathbf{r}_2 \psi^\star_{100}\left(\mathbf{r}_1\right) \psi^\star_{100}\left(\mathbf{r}_2\right) \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \psi_{100}\left(\mathbf{r}_1\right) \psi_{100}\left(\mathbf{r}_2\right) \tag{8}$$

is evaluated as the radial integral only

$$\int r_1^2 dr_1 \int r_2^2 dr_2 R^\star_{10}(r_1) R^\star_{10}(r_2) \frac{e^2}{r_>} R_{10}(r_1) R_{10}(r_2) \tag{9}$$

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8 Calculating the Radial Integral

$$\int r_1^2 dr_1 \int r_2^2 dr_2 R_{10}^\star(r_1) R_{10}^\star(r_2) \frac{e^2}{r_>} R_{10}(r_1) R_{10}(r_2) \tag{10}$$

Radial Part $$R_{1,0}(r) = 2 \cdot \left(\frac{Z}{a_0}\right)^{\frac{3}{2}} \cdot e^{-\frac{Z \cdot r}{a_0}} = R_{1,0}^*(r)$$

Integral:

$$\begin{aligned} & \int_0^\infty \int_0^\infty r_1^2 \cdot r_2^2 \cdot R_{1,0}(r_1)^2 \cdot R_{1,0}(r_2)^2 \frac{e^2}{r_>} dr_1 dr_2 \\ = & \int_0^\infty \int_0^\infty 2^4 \left(\frac{Z}{a_0}\right)^6 e^{-\frac{2Z}{a_0}(r_1+r_2)} r_1^2 \cdot r_2^2 \frac{e^2}{r_>} dr_1 dr_2 \\ = & \, 2^4 \left(\frac{Z}{a_0}\right)^6 \cdot e^2 \int_0^\infty \int_0^\infty e^{-\frac{2Z}{a_0}(r_1+r_2)} r_1^2 \cdot r_2^2 \frac{1}{r_>} dr_1 dr_2 \end{aligned}$$

With substitutions $\frac{2Z}{a_0} r_1 \rightarrow r_1$ and $\frac{2Z}{a_0} r_2 \rightarrow r_2$

$$= \frac{1}{2} \frac{Ze^2}{a_0} \underbrace{\int_0^\infty \int_0^\infty r_1^2 r_2^2 e^{-r_1} e^{-r_2} \frac{1}{r_>} dr_1 dr_2}_{intA} \qquad with \qquad \frac{e^2}{a_0} = 1 a.u. = E_0$$

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We split the integrtion into two integrals. For each r_1 are we taking the integral over r_2 and than can we take the integrale over r_1:

$$\begin{aligned} intA &= \int_0^\infty \left(\int_0^{r_1} e^{-r_1-r_2} r_1 r_2^2 dr_2 \right) dr_1 + \int_0^\infty \left(\int_{r_1}^\infty e^{-r_1-r_2} r_1^2 r_2 dr_2 \right) dr_1 \\ &= \int_0^\infty r_1 e^{-r_1} \underbrace{\int_0^{r_1} r_2^2 e^{-r_2} dr_2}_{intB} dr_1 + \int_0^\infty r_1^2 e^{-r_1} \underbrace{\int_{r_1}^\infty e^{-r_2} r_2 dr_2}_{intC} dr_1 \end{aligned}$$

With partial integration one get:

$$intB = 2 - e^{-r_1}(r_1^2 + 2r_1 + 2)$$

$$intC = e^{-r_1}(r_1 + 1)$$

And with this you get by again merging the two split integrals:

$$intA = \int_0^\infty 2r_1 e^{-r_1} - e^{-2r_1}(r_1^2 + 2r_1) dr_1$$

We use

$$\int_0^\infty x^n e^{-x} dx = n!$$

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If the exponent contains α, we make substitution

$$x = \frac{1}{\alpha} y \qquad\qquad dx = \frac{1}{\alpha}\ dy$$

so that

$$\int_0^\infty \ x^n \ \ dx \ e^{-\alpha x} \ = \ \frac{1}{\alpha^{n+1}} \int_0^\infty \ y^n \ \ dy \ e^{-y}$$

We re-write $intA$ as

$$intA = \int_0^\infty 2r_1 e^{-r_1} dr_1 - \int_0^\infty e^{-2r_1} r_1^2 dr_1 - \int_0^\infty e^{-2r_1} 2r_1 dr_1$$

We see that the first integral has $n = 1$ and no constant in the exponential; thus we get 2. Second term contains $n = 2$ and $\alpha = 2$. It thus gives

$$-\frac{1}{2^3} 2! = \frac{1}{4}$$

The third term has $n = 1$ and $\alpha = 2$. It gives

$$-2\frac{1}{2^2} 1! = \frac{1}{2}$$

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The final expression for

$$A = \int_0^\infty \int_0^\infty r_1^2 r_2^2 e^{-r_1} e^{-r_2} \frac{1}{r_>} dr_1 dr_2 \tag{11}$$

is thus

$$A = 2 - \frac{1}{4} - \frac{1}{2} = \frac{5}{4}$$

And with this the whole integral becomes

$$\int d^3\mathbf{r}_1 \int d^3\mathbf{r}_2 \; \psi_{100}^\star\left(\mathbf{r}_1\right) \psi_{100}^\star\left(\mathbf{r}_2\right) \frac{e^2}{\left|\mathbf{r}_1 - \mathbf{r}_2\right|} \psi_{100}\left(\mathbf{r}_1\right) \psi_{100}\left(\mathbf{r}_2\right) = \frac{5}{8} \frac{Ze^2}{a_0} \tag{12}$$

Acknowledgement: Alexander Sauter (PHYS261 fall 2006) has done lots of work on this part of the document

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Variational methods for quantum mechanics are mainly based on this:

The **functional** $\langle\ \phi\ |H|\ \phi\ \rangle\ \geq\ E_{g.s.}$
it means
$\langle\ \phi\ |H|\ \phi\ \rangle$ has an **absolute minimum** for $|\ \phi\ \rangle\ \rightarrow |\varphi_{g.s.}\rangle$

Suppose we know the exact solutions $|\varphi_\alpha\rangle$ (**ground state** $|\varphi_{g.s.}\rangle$)

$$H\ |\varphi_\alpha\rangle\ =\ E_\alpha\ |\varphi_\alpha\rangle \qquad E_\alpha\ \geq\ E_{g.s.}$$

For any $|\phi\rangle$ - i.e. also any approximation - we can use the expansion

$$|\ \phi\ \rangle\ =\ \sum c_\alpha\ |\varphi_\alpha\rangle \tag{13}$$

$$\langle\ \phi\ |H|\ \phi\ \rangle\ =\ \sum c_\beta^* \sum c_\alpha\ \langle\varphi_\beta|H|\varphi_\alpha\rangle\ =\ \sum c_\beta^* \sum c_\alpha\ E_\alpha \langle\varphi_\beta|\varphi_\alpha\rangle$$

Thus

$$\langle\ \phi\ |H|\ \phi\ \rangle\ =\ \sum |c_\alpha|^2\ E_\alpha \quad \geq\ \sum |c_\alpha|^2\ E_{g.s.}$$

And thus

$$\langle\ \phi\ |H|\ \phi\ \rangle\ \geq\ E_{g.s.} \qquad\qquad \langle\ \phi\ |H|\ \phi\ \rangle\ \geq\ \langle\varphi_{g.s.}|H|\varphi_{g.s.}\rangle$$

As the approximation $|\ \phi\ \rangle$ improves, it approaches $E_{g.s.}$ from above.

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9 The variational method for Helium

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We start with hydrogen-like (one electron) problem

$$H = T_1 + V_1.$$

We remember that the kinetic energy contains only second derivatives of the wave-function, while

$$V_i = -\frac{Ze^2}{r_i}.$$

We know that the ground state energy is (and the wave function)

$$E_{1s}(Z) = -\frac{1}{2}\, Z^2 \frac{e^2}{a_0} \qquad \Psi_{1,0,0}(\mathbf{r}) = \sqrt{\frac{1}{\pi}} \left(\frac{Z}{a_0}\right)^{\frac{3}{2}} \cdot e^{-\frac{Z\cdot r}{a_0}}$$

We avoid unnecessary evaluations by using *virial theorem*. It states:

$$\langle T \rangle = -\frac{1}{2} \langle V \rangle$$

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Since

$$\langle H \rangle \;=\; E_{1s}(Z) \;=\; -\frac{1}{2}\; Z^2 \frac{e^2}{a_0} \;=\; -\frac{1}{2}\; Z^2\; E_0$$

and

$$\langle H \rangle = \langle T \rangle + \langle V \rangle$$

we can see that

$$\langle T \rangle \;=\; \frac{1}{2}\; Z^2\; E_0$$

and

$$\langle V \rangle \;=\; -Z^2\; E_0$$

We introduce a new variable, meaning an unknown effective charge number z, defining the wavefunctions.

When $z \;=\; Z$, the kinetic energy $\langle T \rangle$ is $\frac{1}{2}\; Z^2\; E_0$. As we mentioned, the kinetic energy contains only second derivatives, no Z. That means that when z becomes different from Z, there can only be z in the kinetic energy T result, thus

$$\langle T(z) \rangle \;=\; \frac{1}{2}\; z^2\; E_0$$

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On the other hand, the potential energy contains Z, as seen above. Thus

$$\langle V(z) \rangle \;=\; -\; z\; Z\; E_0$$

We look now at the total energy for two electrons including the repulsion

$$H = T_1 + T_2 + V_1 + V_2 + V_{12}.$$

The repulsion term V_{12} is known for the hydrogen like orbitals, or repulsion between two electrons where both are in $1s$ orbital. For atomic number Z we obtained

$$V_{12} \;=\; \frac{5}{8}\frac{Ze^2}{a_0} \;=\; \frac{5}{8}\; Z\; E_0.$$

Again, there is no Z in the repulsion energy operator, therefore

$$V_{12}(z) \;=\; \frac{5}{8}\; z\; E_0$$

for the orbitals with effective z.

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Thus

$$E(z) \;=\; E_0\left(\frac{1}{2}\;z^2\;\; - zZ\right) + E_0\left(\frac{1}{2}\;z^2\;\; - zZ\right) + E_0\frac{5}{8}z.$$

or

$$E(z) \;=\; \left(z^2 - 2zZ + \frac{5}{8}z\right)E_0.$$

The variational method says that for the ground state the energy functional

$$E(z) \;=\; \left(z^2 - 2zZ + \frac{5}{8}z\right)E_0.$$

must be extremal:

$$\frac{d}{dz}E(z) = 0$$

$$\Leftrightarrow 2z - 2Z + \frac{5}{8} = 0$$

$$\Leftrightarrow z = Z - \frac{5}{16}.$$

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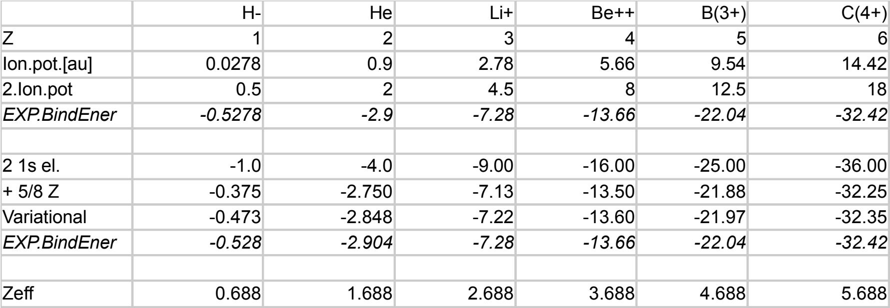

	H-	He	Li+	Be++	B(3+)	C(4+)
Z	1	2	3	4	5	6
Ion.pot.[au]	0.0278	0.9	2.78	5.66	9.54	14.42
2.Ion.pot	0.5	2	4.5	8	12.5	18
EXP.BindEner	*-0.5278*	*-2.9*	*-7.28*	*-13.66*	*-22.04*	*-32.42*
2 1s el.	-1.0	-4.0	-9.00	-16.00	-25.00	-36.00
+ 5/8 Z	-0.375	-2.750	-7.13	-13.50	-21.88	-32.25
Variational	-0.473	-2.848	-7.22	-13.60	-21.97	-32.35
EXP.BindEner	*-0.528*	*-2.904*	*-7.28*	*-13.66*	*-22.04*	*-32.42*
Zeff	0.688	1.688	2.688	3.688	4.688	5.688

Figure 4: Experimental ionization potentials and results of the approximations. Energies given in atomic units

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	H-	He	Li+	Be++	B(3+)	C(4+)
Z	1	2	3	4	5	6
Ion.pot.[eV]	0.757	24.60	75.62	153.95	259.49	392.22
2.Ion.pot	13.600	54.40	122.40	217.60	340.00	489.60
EXP.BindEner	*-14.357*	*-79.00*	*-198.02*	*-371.55*	*-599.49*	*-881.82*
2 1s el.	-27.200	-108.80	-244.80	-435.20	-680.00	-979.20
+ 5/8 Z	-10.200	-74.80	-193.80	-367.20	-595.00	-877.20
Variational	-12.856	-77.46	-196.46	-369.86	-597.66	-879.86
EXP.BindEner	*-14.357*	*-79.00*	*-198.02*	*-371.55*	*-599.49*	*-881.82*
Zeff	0.688	1.688	2.688	3.688	4.688	5.688

Figure 5: Experimental ionization potentials and results of the approximations. Energies given in electronVolts

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	H-	He	Li+	Be++	B(3+)	C(4+)
Z	1	2	3	4	5	6
Ion.pot.[eV]	0.757	24.60	75.62	153.95	259.49	392.22
2.Ion.pot	13.600	54.40	122.40	217.60	340.00	489.60
EXP.BindEner	*-14.357*	*-79.00*	*-198.02*	*-371.55*	*-599.49*	*-881.82*
2 1s el.	-27.200	-108.80	-244.80	-435.20	-680.00	-979.20
+ 5/8 Z	-10.200	-74.80	-193.80	-367.20	-595.00	-877.20
Variational	-12.856	-77.46	-196.46	-369.86	-597.66	-879.86
EXP.BindEner	*-14.357*	*-79.00*	*-198.02*	*-371.55*	*-599.49*	*-881.82*
Zeff	0.688	1.688	2.688	3.688	4.688	5.688

Figure 6: Table of approximation results (in electronVolts)

$$E_{1s}(Z=1) \;=\; -13.6eV \;=\; -0.5E_0$$

($E_0 \;=\; 27.2eV$ is the atomic unit of energy)

$$E_{1s}(Z) \;=\; -Z^2 13.6eV \;=\; -0.5Z^2 \;\; E_0$$

$$\left\langle \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \right\rangle_Z = \frac{5}{8} Z\ E_0 \quad (= 17\ eV\ \ for\ Z=1\ \ = 34\ eV\ \ for\ Z=2\ )$$

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10 Hylleraas variational function for ground state of helium

Our variational method assumed the product function for two electrons.

One can construct various functions where the variables can not be separated into a product

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) \longrightarrow \psi(\mathbf{r}_1)\psi(\mathbf{r}_2) \qquad\qquad \psi_{1,0,0}(\mathbf{r}_i) = \sqrt{\frac{1}{\pi}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} \cdot e^{-\frac{Zr_i}{a_0}}$$

Already in 1929 Norwegian physicist Egil Hylleraas worked with variational method for a "correlated function" of a special type - using transformed coordinates

$$\begin{aligned} (\mathbf{r}_1, \mathbf{r}_2) \longrightarrow s &= r_1 + r_2 & t &= r_1 - r_2 & u &= r_{12} = |\mathbf{r}_1 - \mathbf{r}_2| \\ s &\in (0, \infty) & t &\in (-\infty, \infty) & u &\in (0, \infty) \end{aligned}$$

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) \quad \longrightarrow \quad \psi(s, t, u) = e^{-zs} \sum_{l,m,n=0}^{N} c_{l,2m,n} \; s^l \;\; t^{2m} \;\; u^n$$

The variational parameters here are the constant z and all the coefficients $c_{l,2m,n}$ Note that $e^{-zs} = e^{-zr_1}e^{-zr_2}$ is up to a normalisation the product function with the effective charge number z used in our variational method.

Hylleraas (1929) used 6 variational parameters.

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11 Configuration mixing

Consider the usual:

$$H_x(x)\varphi_\alpha(x) = E_\alpha\varphi_\alpha(x)$$

$$H_y(y)\chi_\beta(y) = E_\beta\chi_\beta(y)$$

For any $\Phi(x)$

$$\Phi(x) = \sum c_\alpha\varphi_\alpha(x)$$

For any $\Xi(x)$

$$\Xi(y) = \sum d_\beta\chi_\beta(y)$$

Take now a general $\Psi(x,y)$. First look at y as a parameter, $\Psi(x,y_0)$

$$\Psi(x,y_0) \to \Phi(x) = \sum c_\alpha(y_0)\varphi_\alpha(x)$$

for every y_0 ; Thus we get a new function of y;

$$c_\alpha(y) = \sum d_\beta(\alpha)\chi_\beta(y)$$

Inserting back:

$$\Psi(x,y) = \sum d_\beta(\alpha)\chi_\beta(y)\varphi_\alpha(x)$$

Or, with a simpler notation

$$\Psi(x,y) = \sum d_{\beta\alpha}\chi_\beta(y)\varphi_\alpha(x)$$

In the case of Helium, for example, the $H(x)$ and $H(y)$ are identical and so are the $\chi_\beta(y)$ and $\varphi_\alpha(x)$. This becomes configuration mixing.

$$\Psi(x,y) = \sum d_{\beta\alpha}\varphi_\beta(y)\varphi_\alpha(x)$$

The coefficients are found by diagonalization.

For three coordinate sets - e.g. for Lithium :

$$\Psi(x,y,z) = \sum D_{\gamma\beta\alpha}\varphi(z)\varphi_\beta(y)\varphi_\alpha(x)$$

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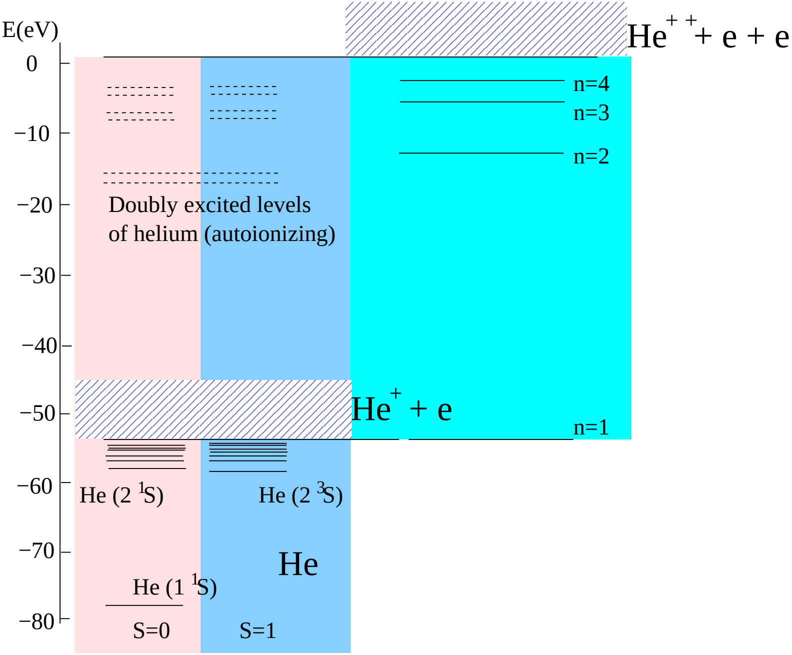

Figure 7: Excited states of helium

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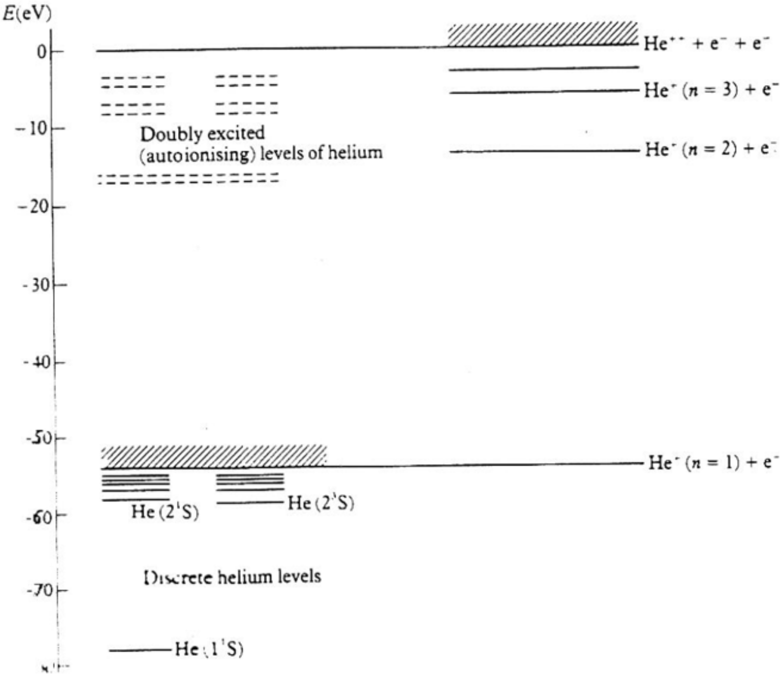

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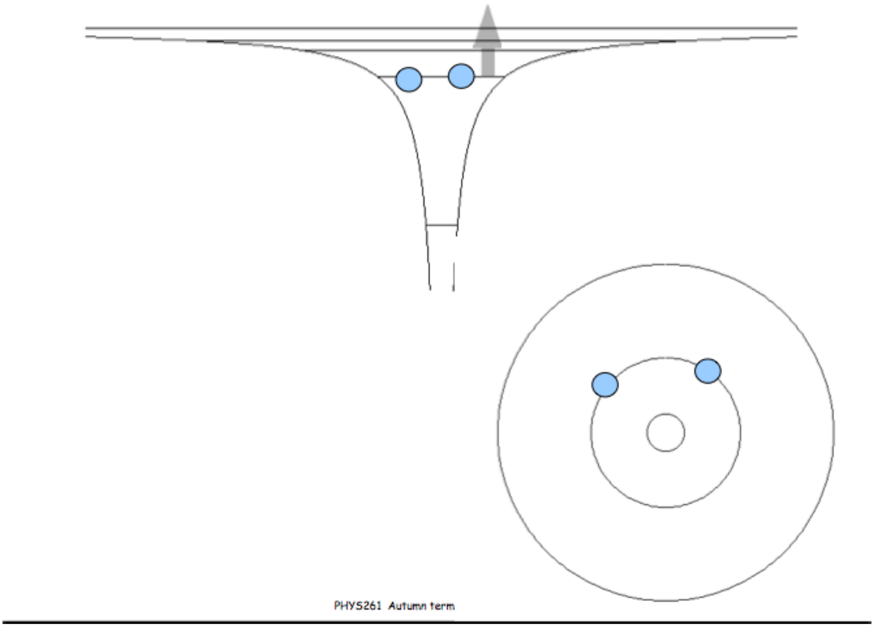

PHYS261 Autumn term

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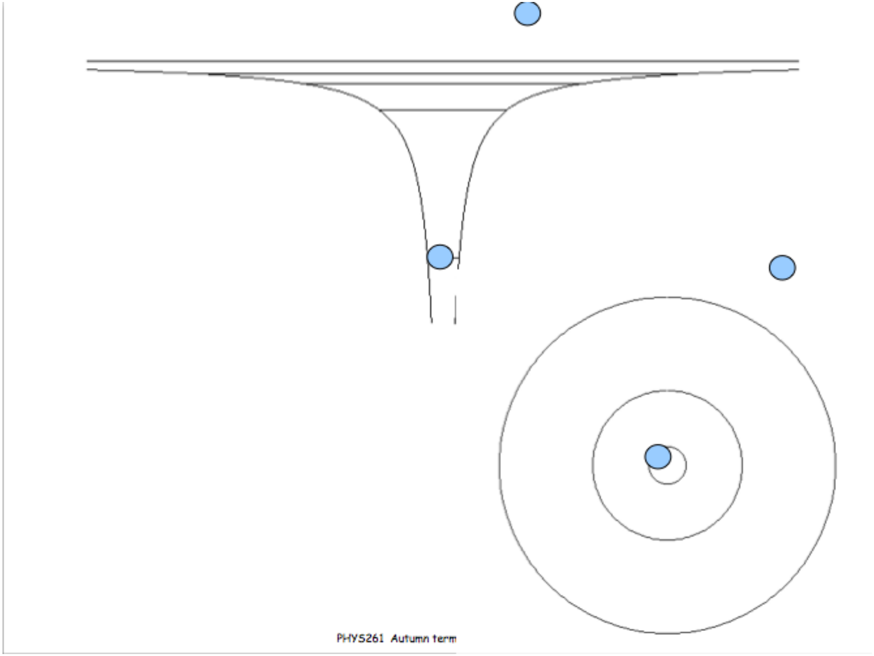

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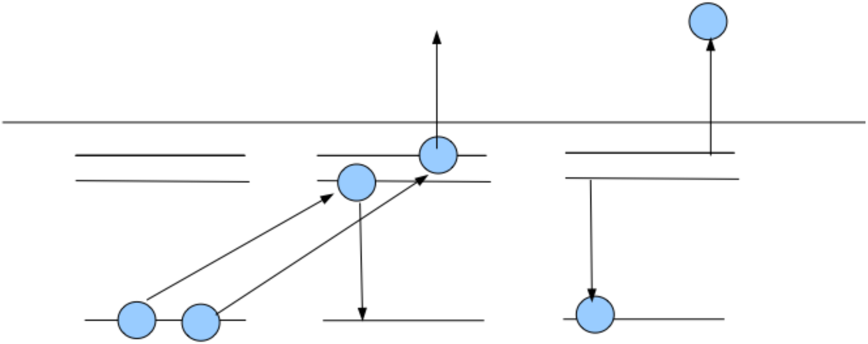

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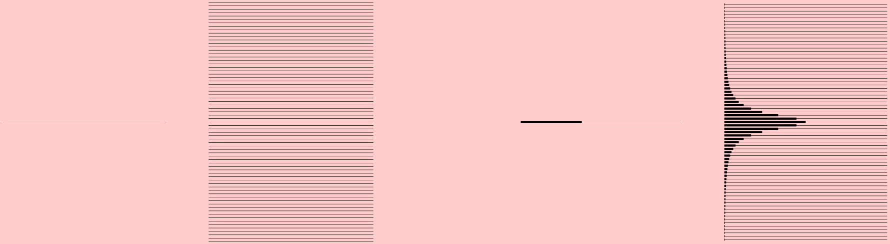
Resonances as discussed in the topic *Light and Atoms*



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12 Atomic Units

Unit of length is the Bohr radius:

$$a_0 = \frac{\hbar^2}{m_e e^2} \left(= 4\pi\epsilon_0 \frac{\hbar^2}{m_e e^2} \right)$$

The first is in atomic units, second in SI-units. This quantity can be remembered by recalling the virial theorem, i.e. that in absolute value, half of the potential energy is equal to the kinetic energy. This gives us

$$\frac{1}{2}\frac{e^2}{a_0} = \frac{\hbar^2}{2m_e {a_0}^2}$$

and if we accept this relation, we have the above value of a_0.

The so called fine structure constant

$$\alpha = \frac{e^2}{\hbar c}$$

expresses in general the *weakness* of electromagnetic interaction.

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Some Constants and Quantities

$v_0 = \alpha c = 2.18710^6$ m s$^{-}1$	Bohr velocity
$a_0 = 0.529177\ 10^{-10}$ m	Bohr radius
$\hbar = 0.6582\ 10^{-15}$ eV s	Planck's constant
$k_B = 0.8625\ 10^{-4}$ eV $^{\circ}$K^{-1}	Boltzmann constant
R $= N_A k_B$	
$N_A = 6.0222\ 10^{23}$	Avogadro's number
$\mu_B = 0.579\ 10^{-4}$ eV (Tesla)$^{-1}$	Bohr magneton

Plank's formula

$$\rho(\omega_{ba}) \ = \ \frac{\hbar\omega_{ba}^3}{\pi^2 c^3} \, \frac{1}{e^{\hbar\omega/kT} - 1}$$

Useful formulae and informations

$P_0\,(cos\theta) = 1$ $\qquad$ $P_1\,(cos\theta) = cos\theta$

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Main Topics

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Calculations from other sources - future extension - must be modified

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Part 1

$$e^{i\mathbf{K}\cdot\mathbf{r}} = 4\pi \sum_{LM} i^L j_L(Kr) Y^*_{LM}(\hat{K}) Y_{LM}(\hat{r}) \tag{14}$$

Part 2

$$\frac{1}{|\mathbf{r_j} - \mathbf{R}(t)|} = \sum_{LM} \frac{4\pi}{2L+1} \frac{r_<^L}{r_>^{L+1}} Y^\star_{LM}(\hat{R}) Y_{LM}(\hat{r}) \tag{15}$$

Part 3

$$V_{fi} =< \Phi_f(\mathbf{r})| \sum_{LM} \frac{4\pi}{2L+1} \frac{r_<^L}{r_>^{L+1}} Y^\star_{LM}(\hat{R}) Y_{LM}(\hat{r}) |\Phi_i(\mathbf{r}) > \tag{16}$$

where

$$r_< = r, \quad r_> = R \quad \text{for} \quad |\mathbf{r}| \ < \ |\mathbf{R}|$$

$$r_< = R, \quad r_> = r \quad \text{for} \quad |\mathbf{r}| \ > \ |\mathbf{R}|$$

then:

$$V_{fi} = < R_f^\star(\mathbf{r}) Y_{l_f m_f}^\star(\hat{r}) | \sum_{LM} \frac{4\pi}{2L+1} \frac{r_<^L}{r_>^{L+1}} Y_{LM}^\star(\hat{R}) Y_{LM}(\hat{r}) | R_i(\mathbf{r}) Y_{l_i m_i}(\hat{r}) > \tag{17}$$

$$V_{fi} = \sum_{LM} \frac{4\pi}{2L+1} \int_0^R r^2 dr \frac{r^L}{R^{L+1}} R_f^\star(\mathbf{r}) [Y_{l_f m_f}^\star(\hat{r}) Y_{LM}^\star(\hat{R}) Y_{LM}(\hat{r})] R_i(\mathbf{r}) Y_{l_i m_i}(\hat{r}) +$$
$$\int_R^\infty r^2 dr \frac{R^L}{r^{L+1}} R_f^\star(\mathbf{r}) [Y_{l_f m_f}^\star(\hat{r}) Y_{LM}(\hat{r}) Y_{LM}^\star(\hat{R})] R_i(\mathbf{r}) Y_{l_i m_i}(\hat{r}) \tag{18}$$

This can be described by a simple notation

$$V_{fi} = \sum_{LM} \frac{4\pi}{2L+1} [G_{fi}^L(R(t))][Y_{LM}^\star(\hat{R})][C^L] \tag{19}$$

where $G_{fi}^L(R(t))$ is called The G-function and C^L is composed of Clebsch-Gordan coefficients. The matrix element is different from zero only if:

$$M = m_i + m_f$$

and

$$|l_i - l_f| \leq L \leq |l_i + l_f|$$

on

$$l_f + L + l_i$$

is even.

As can be seen above, we denote

$$G^L_{fi}[R(t)] = \int_0^\infty R^\star_f(\mathbf{r}) \frac{r^L <}{r^{L+1} >} R_i(\mathbf{r}) r^2 dr =$$
$$\frac{1}{R^{L+1}} \int_0^R r^L r^2 dr R^\star_f(\mathbf{r}) R_i(\mathbf{r}) + R^L \int_R^\infty \frac{1}{r^{L+1}} r^2 dr R^\star_f(\mathbf{r}) R_i(\mathbf{r}) \tag{20}$$

$R_i(\mathbf{r})$ and $R_f(\mathbf{r})$ are the radial wave functions for initial and final states.

The integration over the angular parts, which is the integral over three spherical harmonics, gives

$$C^L = \int Y^\star_{l_f m_f}(\theta,\varphi) Y_{LM}(\theta,\varphi) Y_{l_i m_i}(\theta,\varphi) d\Omega \tag{21}$$

$$(-1)^{m_f}[\frac{(2l_f+1)(2L+1)(2l_i+1)}{4\pi}]^{\frac{1}{2}}$$

$$\begin{pmatrix} l_f & L & l_i \\ -m_f & M & m_i \end{pmatrix} \begin{pmatrix} l_f & L & l_i \\ 0 & 0 & 0 \end{pmatrix}$$

This is known as Gaunts formula, and the numerical values $\begin{pmatrix} a & b & c \\ d & e & f \end{pmatrix}$ are Wigner-3j symbols, up to a factor equal to Clebsch-Gordan coefficients.