

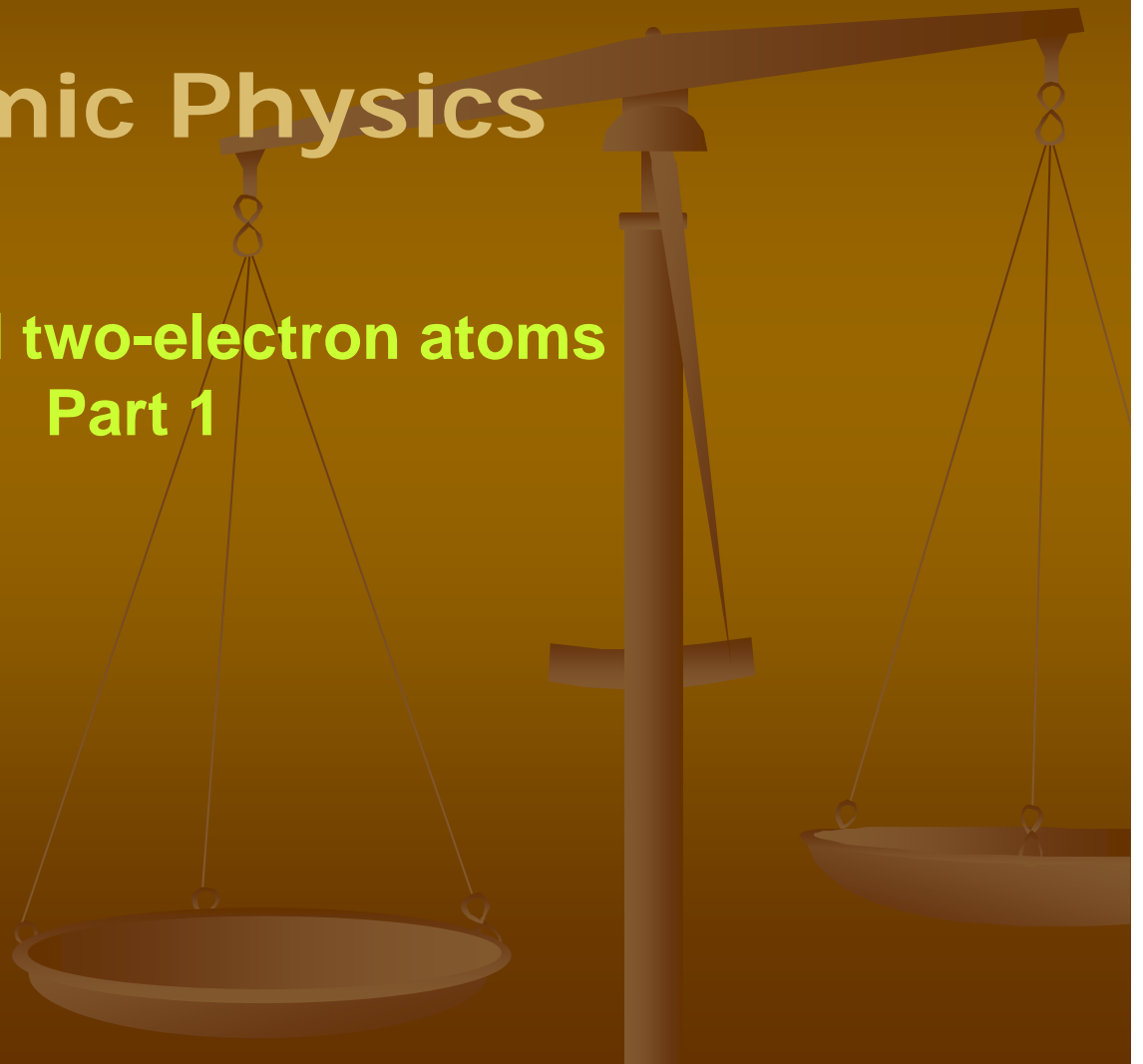
Teaching From the Far Side

- Explain



Atomic Physics

Helium and two-electron atoms Part 1



The helium atom

Work together -

1. Draw an energy level diagram showing all helium excited states.

Label the energy levels... according to

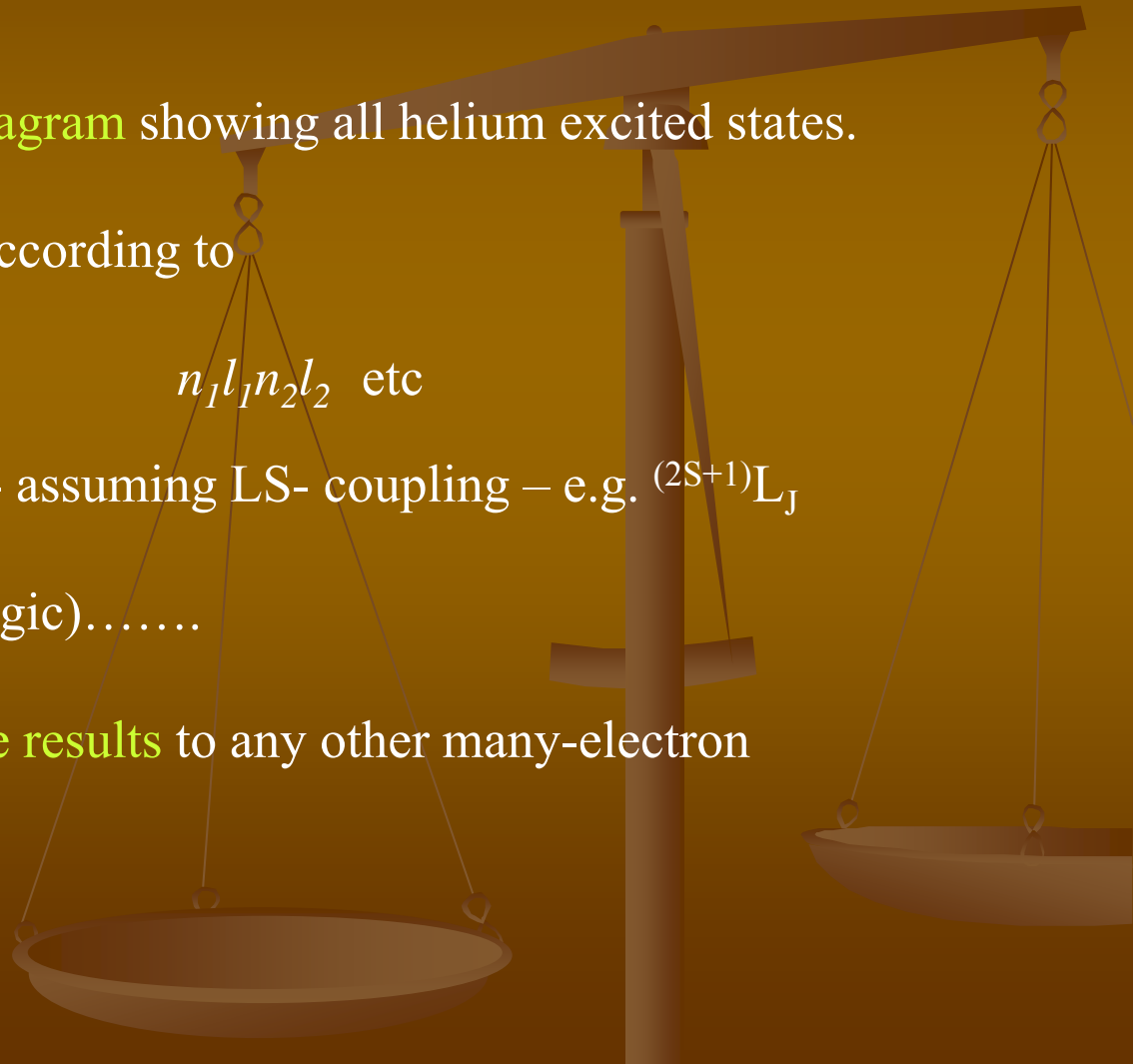
(a) Configurations

$n_1l_1n_2l_2$ etc

(b) Spectroscopic notation - assuming LS- coupling – e.g. $(2S+1)L_J$

Think about systematics (logic).....

2. Can you generalize these results to any other many-electron systems?



EXPERIMENT

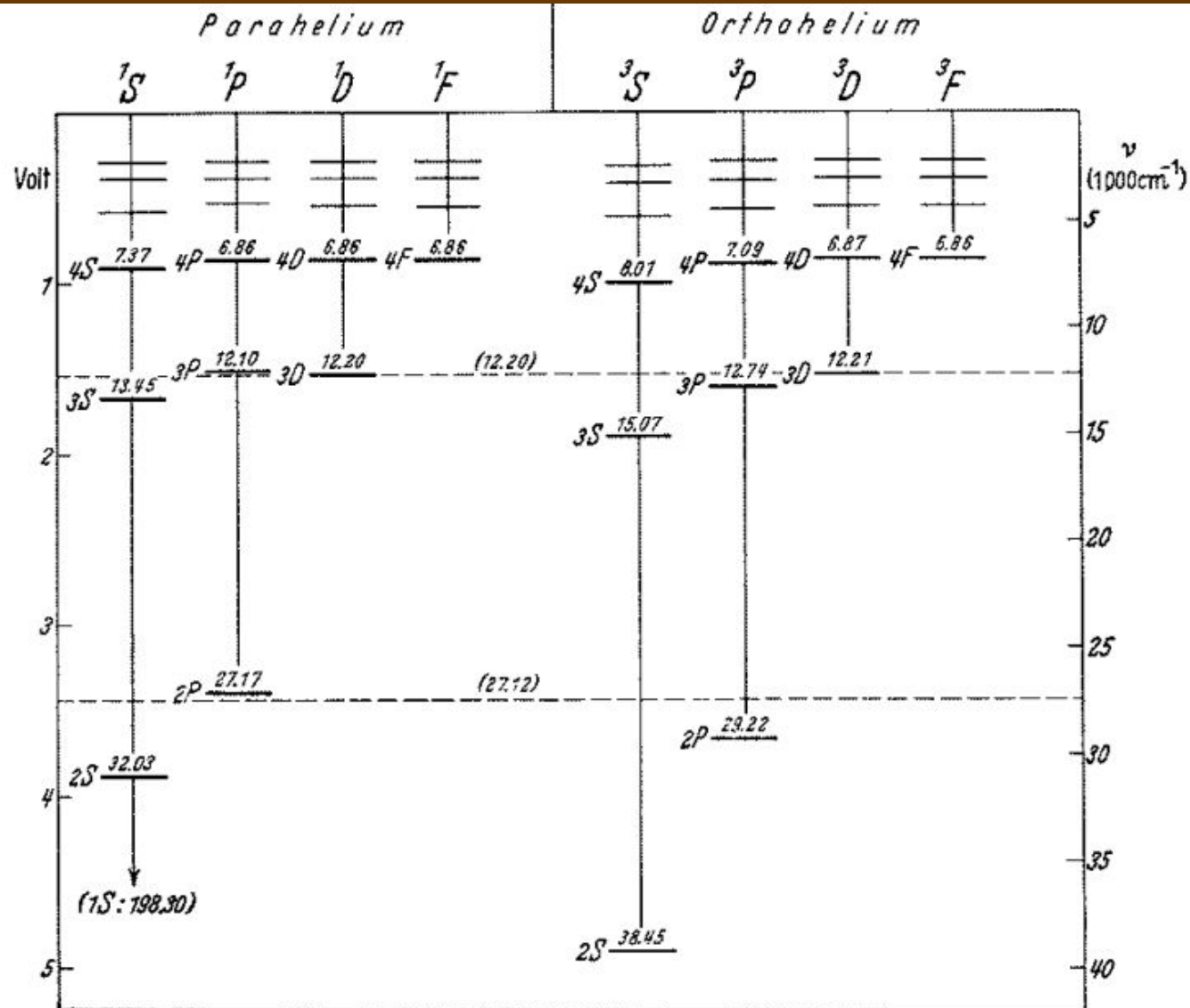


Fig. 15. The experimental energy levels of helium. The scale on the left represents ionization potential in electron volts. The numbers next to the levels are the wave numbers corresponding to the ionization potential, expressed in units of 10^3 cm^{-1} . The dotted lines represent the energy levels of hydrogen (nuclear charge = $Z-1=1$).

Note:

- No $1s1s$
- Singlets
- Triplets
- Hydrogen energies?
- S/T diffs

The basic **2-electron Schrodinger equation**
(just the $1/r$ potentials and the non-relativistic kinetic energies) is:

$$\left\{ -\frac{\hbar^2}{2m} \nabla_1^2 - \frac{\hbar^2}{2m} \nabla_2^2 - \frac{Ze^2}{4\pi\epsilon_0 r_1} - \frac{Ze^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 r_{12}} \right\} \psi = E\psi.$$

or

$$(\mathcal{H}_1 + \mathcal{H}_2 + \mathcal{H}')\psi = E\psi,$$

where

$$\mathcal{H}_1 = -\frac{\hbar^2}{2m} \nabla_1^2 - \frac{Ze^2}{4\pi\epsilon_0 r_1}.$$

and similarly for electron 2, with

$$\mathcal{H}' = e^2/4\pi\epsilon_0 r_{12}.$$

ψ is the wave function for the whole system.

The ground state binding energy

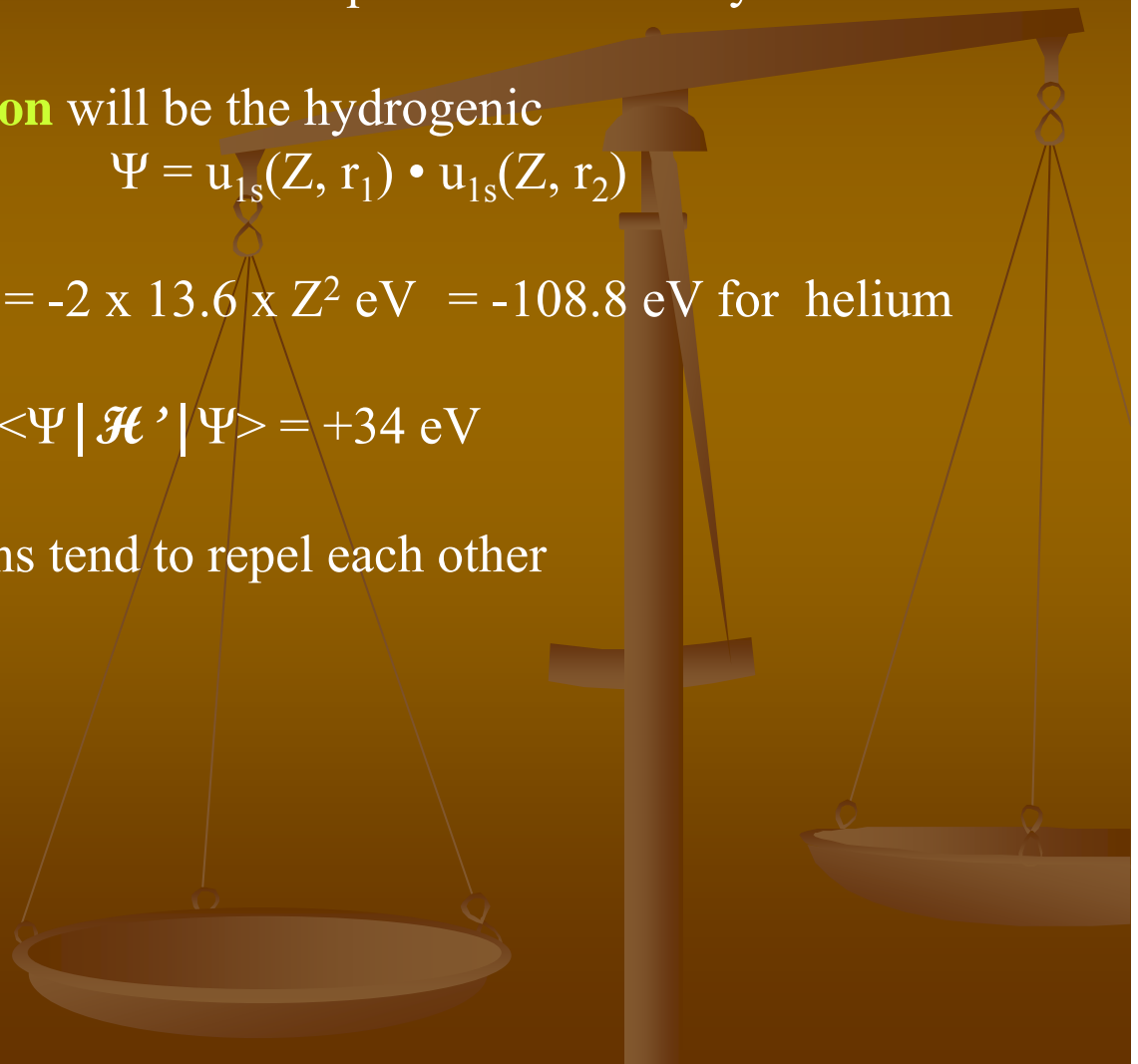
Let $\mathcal{H}_0 = \mathcal{H}_1 + \mathcal{H}_2$, and treat \mathcal{H}' in first order perturbation theory:

Then the **zero order wavefunction** will be the hydrogenic $n=1, Z=2$ wavefunction product: $\Psi = u_{1s}(Z, r_1) \cdot u_{1s}(Z, r_2)$

Zero-order Eigen-energy is $E_0 = -2 \times 13.6 \times Z^2 \text{ eV} = -108.8 \text{ eV}$ for helium

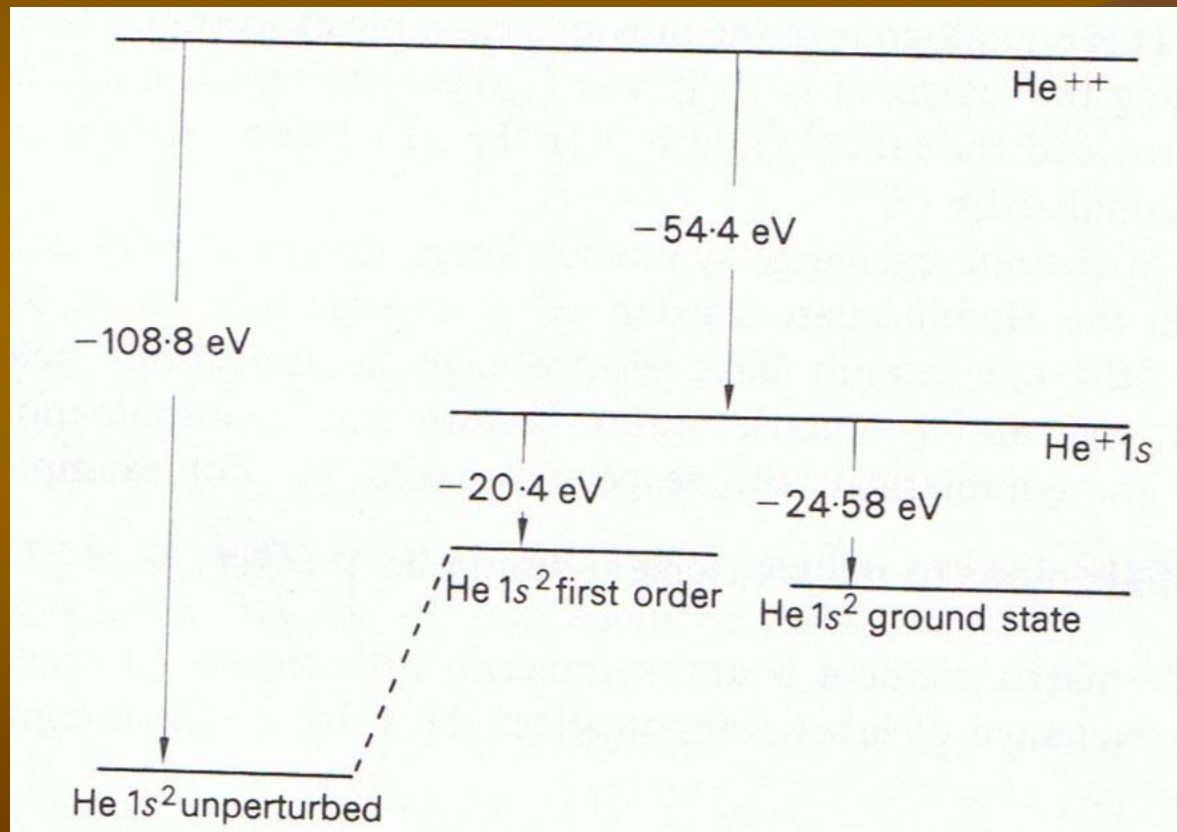
Perturbation energy $\Delta E = \langle \Psi | \mathcal{H}' | \Psi \rangle = +34 \text{ eV}$

NB – it is repulsive – the electrons tend to repel each other



The energy to remove both electrons to infinity is $\{-E_0 + \Delta E\} = 74.8 \text{ eV}$
But we know the energy to remove the 2nd electron is $Z^2 \times 13.6 = 54.4 \text{ eV}$

Hence, the first ionization potential = $74.8 - 54.4 = 20.4 \text{ eV}$ {Expt = 24.58 eV }



Homework Problem: Show that $\Delta E = +34 \text{ eV}$ [$= (5/4) \times Z \times 13.6 \text{ eV}$]

Helium excited states

“**All**” configurations have just one electron excited...

e.g One electron in the 1s state: $u_{1s}(1) = R_{1s}(r_1) \cdot 1/\sqrt{4\pi}$

2nd electron in the nl state : $u_{nl}(2) = R_{nl}(r_2) \cdot Y_{lm}(\theta_2, \phi_2)$

BUT: since electrons are identical Fermi particles...

Two spatial linear combinations of the 2 electrons are allowed – symmetric and antisymmetric – Ψ^S and Ψ^A

- The total wavefunction including spin must be antisymmetric
- thus the spin part of the ground state must have an antisymmetric spin state ($S=0$)
- The excited states can have both symmetric and antisymmetric spins ($S=1$ & $S=0$)
- And the excited state spatial parts can be written:

$$\Psi^S(\text{spatial}) = (1/\sqrt{2}) \cdot \{u_{1s}(1) u_{nl}(2) + u_{1s}(2) u_{nl}(1)\} \quad \text{singlet spin}$$

$$\Psi^A(\text{spatial}) = (1/\sqrt{2}) \cdot \{u_{1s}(1) u_{nl}(2) - u_{1s}(2) u_{nl}(1)\} \quad \text{triplet spin}$$

Spin wavefunctions

Total wavefunctions are:

$$\begin{aligned} \Psi \text{ (singlet)} &= \Psi_{\text{space}}^S \Psi_{\text{spin}}^A \\ \text{and} \quad \Psi \text{ (triplet)} &= \Psi_{\text{space}}^A \Psi_{\text{spin}}^S \end{aligned}$$

And we write the spin states as:

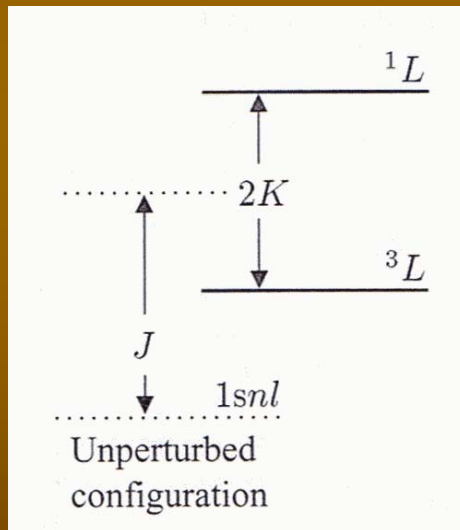
$$\psi_{\text{spin}}^A = \frac{1}{\sqrt{2}} \{ |\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle \},$$

$$\begin{aligned} \psi_{\text{spin}}^S &= |\uparrow\uparrow\rangle \\ &= \frac{1}{\sqrt{2}} \{ |\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle \} \\ &= |\downarrow\downarrow\rangle, \end{aligned}$$

Exchange energy

Treating H' as a perturbation now leads to a different energy change for each of the states $\Delta E = J \pm K$

Where J and K are called the direct and exchange integrals...



$$J = \frac{1}{4\pi\epsilon_0} \iint |u_{1s}(1)|^2 \frac{e^2}{r_{12}} |u_{nl}(2)|^2 dr_1^3 dr_2^3$$

$$K = \frac{1}{4\pi\epsilon_0} \iint u_{1s}^*(1)u_{nl}^*(2) \frac{e^2}{r_{12}} u_{1s}(2)u_{nl}(1) dr_1^3 dr_2^3 .$$

Note: Triplet is lower in energy than the singlet
This is called Hund's rule – highest spin state has the lowest energy

The Direct & Exchange integrals

Example – the **1s2p** singlet and triplet states of helium

Assume that the 1s electron sees a nuclear charge $Z=2$, and the 2p electron is completely outside the 1s wavefunction, and sees $Z=1$

Then let $H_{0a} = -\hbar^2/2m (\nabla_1^2 + \nabla_2^2) - e^2/4\pi\epsilon_0 (2/r_1 + 1/r_2)$

and $H_a' = e^2/4\pi\epsilon_0 (1/r_{12} - 1/r_2)$ NB this goes to zero as $r_2 \rightarrow$ infinity

The Direct integral is then

$$J_{1snl} = e^2/4\pi\epsilon_0 \iint (1/r_{12} - 1/r_2) |u_{1s}(1)|^2 |u_{nl}(2)|^2 d^3\mathbf{r}_1 d^3\mathbf{r}_2 \quad \text{over all space}$$

$$= e^2/4\pi\epsilon_0 \int_0^\infty \int_0^\infty J(r_1, r_2) R_{10}^2(r_1) R_{nl}^2(r_2) r_1^2 dr_1 r_2^2 dr_2 \quad \text{2 radial integrals 0 to } \infty$$

where $J(r_1, r_2)$ is the tricky angular part.....

We need to expand $1/r_{12}$ in spherical harmonics – tedious, but the integrals are known....

The angular parts (direct) ...

$$J(r_1, r_2) = \int_0^{2\pi} \int_0^\pi \int_0^{2\pi} \int_0^\pi \left(\frac{1}{r_{12}} - \frac{1}{r_2} \right) \frac{1}{4\pi} |Y_{lm}(\theta_2, \phi_2)|^2 \\ \times \sin \theta_1 d\theta_1 d\phi_1 \sin \theta_2 d\theta_2 d\phi_2 .$$

Expanding $1/r_{12}$ [for $r_2 > r_1$, and the reverse when $r_1 > r_2$]

$$\frac{1}{r_{12}} = \frac{1}{r_2} \sum_{k=0}^{\infty} \left(\frac{r_1}{r_2} \right)^k \frac{4\pi}{2k+1} \sum_{q=-k}^k Y_{k,q}^*(\theta_1, \phi_1) Y_{k,q}(\theta_2, \phi_2)$$

Only the $k=0$ term survives,
(orthogonality of Y_{lm} s)..to give

$$J(r_1, r_2) = \begin{cases} 0 & \text{for } r_1 < r_2, \\ 1/r_1 - 1/r_2 & \text{for } r_1 > r_2. \end{cases}$$

For $r_1 > r_2$, potential difference is
($2/r_2 + 1/r_1$) - ($-2/r_1 - 1/r_2$) = ($1/r_1 - 1/r_2$)

$$J_{1snl} = \frac{e^2}{4\pi\epsilon_0} \int_0^\infty \left\{ \int_{r_2}^\infty \left(\frac{1}{r_1} - \frac{1}{r_2} \right) R_{10}^2(r_1) r_1^2 dr_1 \right\} R_{nl}^2(r_2) r_2^2 dr_2$$

The exchange integrals

These integrals have the same form as before, but with the 2 values of $Z=2$, and $Z=1$

$$K_{1snl} = \frac{e^2}{4\pi\epsilon_0} \iint K(r_1, r_2) R_{1s}(r_1) R_{nl}(r_1) R_{1s}(r_2) R_{nl}(r_2) r_1^2 dr_1 r_2^2 dr_2$$

Where the angular part is...

$$K(r_1, r_2) = \iiint \frac{1}{r_{12}} Y_{lm}^*(\theta_1, \phi_1) \frac{1}{4\pi} Y_{lm}(\theta_2, \phi_2) \times \sin \theta_1 d\theta_1 d\phi_1 \sin \theta_2 d\theta_2 d\phi_2 .$$

For p-states, only $k=1$ survives, giving

$$K(r_1, r_2) = \begin{cases} r_1/3r_2^2 & \text{for } r_1 < r_2 , \\ r_2/3r_1^2 & \text{for } r_2 < r_1 . \end{cases}$$

Results: $J_{1s2p} = -0.028 \text{ eV}$ (ie. Very little incomplete screening!)

$K_{1s2p} = +.105 \text{ eV}$ (Expt = 0.125 eV)

Not as good for the 1s2s states – screening is not as complete!

Improving on first order perturbation theory

1 – Go to higher orders.....

Advantage – good for all atoms

Disadvantage - Tedious and not very accurate – slow convergence

(Converges to wrong value – h-orbitals are NOT a complete set)

2 – Variational calculation: parametrize the wavefunction and minimize the energy with respect to the parameter(s)

Advantage – very accurate, fast convergence with more parameters

Disadvantage – Tedious, not possible for other atoms (more than 2 electrons)

Let's look at variational calculations...

First done by Hylleraas in 1930 for helium – a landmark set of papers...

(see website)

Wewill begin with calculational method in Bethe and Salpeter

Bethe &
Salpeter,
Pp. 122..

β) *Variation perturbation theory.* Consider a general HAMILTONIAN equation

$$(H_0 + \lambda H_1 - E) u = 0, \quad (25.5)$$

where H_0 and H_1 are any two HERMITIAN operators and λ is considered as a small parameter. We consider the eigenfunction u and eigenvalue E expanded in powers of this parameter,

$$E = \sum_{n=0}^{\infty} \lambda^n E_n, \quad u = \sum_{n=0}^{\infty} \lambda^n U_n. \quad (25.6)$$

If we substitute these expansions into (25.5) and equate the coefficient of each power of λ to zero, we get an infinite set of coupled linear equations,

$$H_0 U_0 - E_0 U_0 = 0, \quad (25.7)$$

$$H_0 U_1 + H_1 U_0 - E_0 U_1 - E_1 U_0 = 0, \quad (25.8)$$

$$H_0 U_2 + H_1 U_1 - E_0 U_2 - E_1 U_1 - E_2 U_0 = 0, \quad (25.9)$$

.....

$$H_0 U_n + H_1 U_{n-1} - \sum_{m=0}^n E_m U_{n-m} = 0.$$

We call (25.7) the unperturbed (or zero order) HAMILTONIAN equation. This equation, like the full Eq. (25.5), has a whole spectrum of solutions. We consider one *particular* solution and consider U_0 and E_0 as known completely and U_0 normalized. Multiply (25.7) by U_1 , (25.8) by U_0 , subtract the two equations and integrate over all space¹. One then obtains the well-known expression for E_1 , the first order perturbation energy,

$$E_1 = \int U_0 H_1 U_0 d\tau. \quad (25.10)$$

A knowledge of the zero-order wave function U_0 , for one particular state alone, thus yields both E_0 and E_1 for this state.

In Eq. (25.8) for the particular state we are considering, the constants E_0 and E_1 and the function U_0 are now known. (25.8) is then an inhomogeneous differential equation for U_1 , which does not contain any unknown eigenvalue. Since U_1 must satisfy some definite boundary conditions (conditions of “good behavior”), the Eq. (25.8) determines the function U_1 for the particular state *uniquely*², at least *in principle*. We shall discuss practical methods of solving for

¹ We restrict ourselves to the case of real functions U_0, U_1, U_2 , etc. for the sake of simplicity.

² Except for an additive multiple of U_0 . The normalization, etc., can be so arranged that U_1 (and U_2 , etc.) is orthogonal to U_0 .

U_1 in a moment. Once U_1 has been found, both E_2 and E_3 can be evaluated as follows. Multiplying (25.7) by U_2 , (25.9) by U_0 , subtracting the equations and integrating, we get

$$E_2 = \int U_0 H_1 U_1 d\tau, \quad (25.11)$$

where we have assumed the normalization such that U_0 and U_1 are orthogonal. Next multiply (25.7) by $-U_3$, (25.8) by $-U_2$, (25.9) by $+U_1$ and the next equation by $+U_0$. Adding these equations and integrating gives

$$E_3 = \int (U_1 H_1 U_1 - E_1 U_1^2) d\tau. \quad (25.12)$$

After E_2 and U_1 have been found, the Eq. (25.9) determines the function U_2 (in principle), and so on. In general, after each additional wave function (e.g. U_2) has been found, *two* additional eigenvalues (e.g. E_4 and E_5) can be evaluated.

Variational techniques - 1

The helium ground state energy:

We can assume some parametric form for the wavefunction, evaluate the Hamiltonian, and then minimize the energy with respect to these parameters

The Ritz/Hylleraas variational method

Simplest idea for the 1s2s helium-like state: guess a 1-parameter (σ) wavefunction

let $\Psi = \exp(\{-(Z-\sigma)(r_1+r_2)\}) = \exp(\{-(Z-\sigma)s\})$ where $s = (r_1+r_2)$

And rewrite the Hamiltonian:

$$\left\{ -\frac{\hbar^2}{2m} \nabla_1^2 - \frac{\hbar^2}{2m} \nabla_2^2 - \frac{Ze^2}{4\pi\epsilon_0 r_1} - \frac{Ze^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 r_{12}} \right\} \psi = E\psi.$$

In terms of s , $t = r_1 - r_2$ and $u = r_{12}$ and then minimize $E = \langle \Psi | \mathcal{H} | \Psi \rangle / \langle \Psi | \Psi \rangle$

-See Bethe & Salpeter, pp. 146-148 for details

-Result – the screening parameter $\sigma = 5/16$, and thus the energy is

- $E = -2(Z-5/16)^2$ Rydbergs

-And the 1st ionization potential $IP = -(E - Z^2) = (Z^2 - 5Z/4 + 25/128)$ Rydbergs

-Note: this is very similar to earlier result – extra term brings it closer to experiment – especially as Z gets larger – for Li^+ , Be^{2+} The isoelectronic sequence

Variational techniques - 2

Hylleraas (1929 and onwards) expanded these ideas to include more parameters..

e.g. wavefunctions which included the exponent σ , and power expansions of s , t and u

$$\text{e.g. } \Psi = \exp\{-(Z-\sigma)s\} \sum s^x t^y u^z \quad x, y, z = 0, 1, 2, 3 \dots$$

With 6 parameters he obtained an ionization potential to 1 part in 10^4 . Using computers Pekeris et al (1958) extended these results to excited S and P states – e.g. thousands of parameters... giving EXACT non-relativistic energies.

Note : that leaves relativistic corrections – (we will treat them later...)

A good overview of the technique, developing a 3-parameter function:
Bhattacharya et al, J. Phys. B 29, L147 (1996)

Examples of early calculations

(1 a.u. = 2 Ry
= 27.2 eV)

1 ¹S and 2 ³S States of Helium

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(Received April 15, 1959)

The method described previously for the solution of the wave equation of two-electron atoms has been applied to the 1 ¹S and 2 ³S states of helium, with the purpose of attaining an accuracy of 0.001 cm⁻¹ in the nonrelativistic energy values. For the 1 ¹S state we have extended our previous calculations by solving determinants of orders 252, 444, 715, and 1078, the last yielding an energy value of -2.903724375 atomic units, with an estimated error of the order of 1 in the last figure. Applying the mass-polarization and relativistic corrections derived from the new wave functions, we obtain a value for the ionization energy of 198 312.0258 cm⁻¹, as against the value of 198 312.011 cm⁻¹ derived previously from the solution of a determinant of order 210. With a Lamb shift correction of -1.339, due to Kabir, Salpeter, and Sucher, this leads to a theoretical value for the ionization energy of 198 310.687 cm⁻¹, compared with Herzberg's experimental value of 198 310.8₂ ± 0.15 cm⁻¹.

For the 2 ³S state we have solved determinants of orders

125, 252, 444, and 715, the last giving an energy value of -2.17522937822 a.u., with an estimated error of the order of 1 in the last figure. This corresponds to a nonrelativistic ionization energy of 38 453.1292 cm⁻¹. The mass-polarization and relativistic corrections bring it up to 38 454.8273 cm⁻¹. Using the value of 74.9 ry obtained by Dalgarno and Kingston for the Lamb-shift excitation energy K_0 , we get a Lamb-shift correction to the ionization energy of the 2 ³S state of -0.16 cm⁻¹. The resulting theoretical value of 38 454.66 cm⁻¹ for the ionization potential is to be compared with the experimental value, which Herzberg estimates to be 38 454.73 ± 0.05 cm⁻¹. The electron density at the nucleus $D(0)$ comes out 33.18416, as against a value of 33.18388 ± 0.00023 which Novick and Commins deduced from the hyperfine splitting. We have also determined expectation values of several positive and negative powers of the three mutual distances, which enter in the expressions for the polarizability and for various sum rules.

Two-Electron Atoms. I. Perturbation Study of the Ground State

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(Received May 3, 1962)

A variational perturbation method used by Hylleraas has been extended to include 70-term basis sets as approximations to the first-order wave function of the two-electron atomic species. An upper limit of -0.15766625⁺ a.u. has been found for the second-order perturbation energy coefficient. It is estimated that this value is converged to at least two units in the seventh decimal place. A value of the third-order perturbation energy coefficient of 0.00869868 a.u. is calculated from the same variational first-order wave function. A number of expectation values to first-order for certain operators [e.g., $\delta(\mathbf{r}_1)$, $\delta(\mathbf{r}_{12})$, p_1^4 , r_1^n , $\cos\theta_{12}$, etc.] are computed, and compared, where possible, to known values. A variety of basis sets is studied, including a set that contains negative powers of the metric variables ("Kinoshita" type) and one that contains only positive powers ("Hylleraas" type). A scheme is proposed that uses first and higher order expectation values for the analysis and characterization of approximate wave functions. This scheme, which is not restricted to two electrons, also opens the possibility of a nonenergetic variational procedure for obtaining wave functions.

A “modern” example...

J. Phys. B: At. Mol. Opt. Phys. **29** (1996) L147–L150. Printed in the UK

LETTER TO THE EDITOR

Analytical approach to the helium-atom ground state using correlated wavefunctions

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Abstract. A realistic three-parameter correlated wavefunction is used to construct an exact analytical expression for the expectation value of the helium-atom Hamiltonian expressed in the interparticle coordinates. The parameters determined variationally are found to satisfy the orbital and correlation cusp conditions to a fair degree of accuracy and yield a value for the ground-state energy which is in good agreement with the exact result.

In terms of interelectronic coordinates, equation (1) for the case of S-states can be written in the form (Roothaan and Weiss 1960)

$$(H - \epsilon)\psi(r_1, r_2, r_{12}) = 0 \quad (2)$$

where

$$H = H_1 + H_2 + H_{12} + H'_{12} \quad (3)$$

with

$$H_j = -\frac{1}{2} \left(\frac{\partial^2}{\partial r_j^2} + \frac{2}{r_j} \frac{\partial}{\partial r_j} \right) - \frac{2}{r_j} \quad (4a)$$

$$H_{12} = - \left(\frac{\partial^2}{\partial r_{12}^2} + \frac{2}{r_{12}} \frac{\partial}{\partial r_{12}} \right) + \frac{1}{r_{12}} \quad (4b)$$

and

$$H'_{12} = - \left(\frac{r_1^2 - r_2^2 + r_{12}^2}{2r_1 r_{12}} \frac{\partial}{\partial r_1} + \frac{r_2^2 - r_1^2 + r_{12}^2}{2r_1 r_{12}} \frac{\partial}{\partial r_2} \right) \frac{\partial}{\partial r_{12}} \quad (4c)$$

The vector operator del implied in (4) is given by (Hylleraas 1964)

$$\nabla_j = \hat{r}_j \frac{\partial}{\partial r_j} + \hat{r}_{12} \frac{\partial}{\partial r_{12}} \quad (5)$$

The ground-state energy for (1) is given by

$$\epsilon = \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} \quad (6)$$

The expectation value of the Hamiltonian can be written in the explicit form

$$\begin{aligned} \langle \psi | H | \psi \rangle = & -\frac{1}{2} \iint (|\nabla_1 \psi|^2 + |\nabla_2 \psi|^2) dr_1 dr_2 - 2 \iint \psi^* \left(\frac{1}{r_1} + \frac{1}{r_2} \right) \psi dr_1 dr_2 \\ & + \iint \psi^* \frac{1}{r_{12}} \psi dr_1 dr_2. \end{aligned} \quad (7)$$

For calculating the ground-state energy of helium by means of (6) and (7), we have chosen to work with the trial wavefunction (Hartree and Ingman 1933)

$$\psi(r_1, r_2, r_{12}) = e^{-\alpha(r_1+r_2)} \chi(r_{12}) \quad (8)$$

where the correlation function

$$\chi(r_{12}) = 1 - \lambda e^{-\mu r_{12}}. \quad (9)$$

The adjustable parameters of our trial wavefunction are α , λ and μ . As $r_{12} \rightarrow \infty$, $\chi(r_{12}) \rightarrow 1$. This expresses the separability of the wavefunction when the two electrons are far apart. As demanded by Hartree and Ingman (1933), we can allow $\chi(r_{12})$ to assume a small finite value for $r_{12} = 0$. Thus our choice for the wavefunction (8) is based on physically founded assumptions. In the mid 1980s, Abbott and Maslen (1986) envisaged a study similar to ours in terms of a correlated wavefunction of the form $\psi(r_1, r_2, r_{12}) = e^{-\xi(r_1+r_2)} e^{\nu r_{12}}$. This choice was originally made by Hylleraas (1929) and rejected subsequently by Hartree and Ingman (1933) as unphysical. When the cusp conditions (Roothaan and Weiss 1960)

$$\left(\frac{1}{\psi} \frac{\partial \psi}{\partial r_1} \right)_{r_1=0} = \left(\frac{1}{\psi} \frac{\partial \psi}{\partial r_2} \right)_{r_2=0} = -Z \quad (10a)$$

and

$$\left(\frac{1}{\psi} \frac{\partial \psi}{\partial r_{12}} \right)_{r_{12}=0} = \frac{1}{2} \quad (10b)$$

are satisfied, the wavefunctions gave a found-state energy -2.8555 au in contrast to the exact value -2.9037 au. Interestingly, if the conditions in (10) are relaxed by allowing $Z \rightarrow Z - 0.14$ and $\gamma = 0.26$, an improved result of -2.8896 au could be obtained. As opposed to the wavefunctions used by Abbott and Maslen (1986), the continuum distorted wavefunction (CDW) of Pluvinaige (1950) is based on a perfectly legitimate physical assumption that the correlation energy arises from a repulsive Coulomb potential which can support continuous spectrum only. But the use of CDW does not permit an analytical approach to the problem and also it gives a poor ground-state energy of -2.8780 au.

To construct an expression for $\langle \psi | H | \psi \rangle$ by using the wavefunction in (8), one would, ideally, like to calculate the integrals involved by the use of well known Hylleraas coordinates $u = r_{12}$, $s = r_1 + r_2$ and $t = r_1 - r_2$. Unfortunately, this approach does not lead to an analytical expression for the energy expectation value (Morse and Feshbach 1953). We thus take recourse to the use of the Fourier transforms (Deb 1994)

$$\frac{e^{-\lambda r}}{r} = \frac{1}{2\pi^2} \int \frac{e^{ip \cdot r}}{(\lambda^2 + p^2)} dp \quad (11)$$

and

$$\frac{1}{r_{12}} = \frac{1}{2\pi^2} \int \frac{e^{iR \cdot (r_1 - r_2)}}{R^2} dR. \quad (12)$$

For $\langle \psi | \psi \rangle$ and $\langle \psi | H | \psi \rangle$ we have found that

$$\langle \psi | \psi \rangle = \frac{\pi^2}{\alpha^3} \left[\frac{1}{\alpha^3} - \frac{2\lambda}{(\mu + 2\alpha)^5} (\mu^2 + 10\mu\alpha + 32\alpha^2) + \frac{\lambda^2}{8(\mu + \alpha)^5} (\mu^2 + 5\mu\alpha + 8\alpha^2) \right] \quad (13)$$

and

$$\langle \psi | H | \psi \rangle = A - B + C \quad (14)$$

with

$$A = \frac{\pi^2}{\alpha^3} \left[\frac{1}{\alpha} - \frac{2\lambda\alpha^2}{(\mu + 2\alpha)^5} (3\mu^2 + 30\mu\alpha + 32\alpha^2) + \frac{\lambda^2}{8(\mu + \alpha)^5} (\mu^4 + 5\mu^3\alpha + 11\mu^2\alpha^2 + 15\mu\alpha^3 + 8\alpha^4) \right] \quad (15a)$$

$$B = \frac{\pi^2}{\alpha^3} \left[\frac{4}{\alpha^2} - \frac{16\lambda\alpha}{(\mu + 2\alpha)^4} (\mu + 8\alpha) + \frac{\lambda^2\alpha}{(\mu + \alpha)^4} (\mu + 4\alpha) \right] \quad (15b)$$

and

$$C = \frac{\pi^2}{\alpha^3} \left[\frac{5}{8\alpha^2} - \frac{\lambda}{(\mu + 2\alpha)^4} (\mu^2 + 8\mu\alpha + 20\alpha^2) + \frac{\lambda^2}{8(\mu + \alpha)^4} (\mu^2 + 4\mu\alpha + 5\alpha^2) \right]. \quad (15c)$$

Minimizing the energy with respect to variations in the parameters of $\psi(r_1, r_2, r_{12})$ we get $\alpha = 1.8395$, $\lambda = 0.586$ and $\mu = 0.379$. For these parameters the correlation cusp condition (10b) comes out to be 0.5365 which is not far from the exact value and, more significantly, the ground-state energy is found to be -2.8894 au. Very recently, Tripathy

Note: Using the Fourier transforms allowed an analytical solution; With just 3 parameters, the result is within 0.3% for the total energy