

Chapter 10

Ground State of the He Atom – 1s State

First order perturbation theory

Neglecting translation of the entire atom.

$$\underline{H} = -\frac{\hbar^2}{2m_0} \nabla_1^2 - \frac{\hbar^2}{2m_0} \nabla_2^2 - \frac{Ze^2}{4\pi\epsilon_0 r_1} - \frac{Ze^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 r_{12}}$$

kinetic energies attraction of electrons to nucleus electron – electron repulsion

1 - electron 1

2 - electron 2

r_1 - distance of 1 to nucleus

r_2 - distance of 2 to nucleus

r_{12} - distance between two electrons

Substituting

$$a_0 = \frac{\epsilon_0 \hbar^2}{\pi m_0 e^2} \quad \text{Bohr radius}$$

$$r_1 = a_0 R_1$$

$$r_2 = a_0 R_2 \quad \text{Distances in terms of Bohr radius}$$

$$r_{12} = a_0 R_{12}$$

$$\frac{\partial^2}{\partial x_1^2} = \frac{1}{a_0^2} \frac{\partial^2}{\partial X_1^2}, \text{ etc.} \quad \text{spatial derivatives in units of Bohr radius}$$

Gives

$$\underline{H} = -\frac{\hbar^2}{2m_0} \frac{1}{a_0^2} (\nabla_1^2 + \nabla_2^2) - \frac{Ze^2}{4\pi\epsilon_0 a_0 R_1} - \frac{Ze^2}{4\pi\epsilon_0 a_0 R_2} + \frac{e^2}{4\pi\epsilon_0 a_0 R_{12}}$$

In units of

$$\frac{e^2}{4\pi\epsilon_0 a_0} \quad \left(-\frac{1}{2} \frac{e^2}{4\pi\epsilon_0 a_0} \Rightarrow \text{ground state, 1s, energy of H atom} \right)$$

$$\underline{H} = -\frac{1}{2}(\nabla_1^2 + \nabla_2^2) - \frac{Z}{R_1} - \frac{Z}{R_2} + \frac{1}{R_{12}}$$

(Nothing changed. Substitutions simplify writing equations.)

Take

$$\underline{H}^0 = -\frac{1}{2}(\nabla_1^2 + \nabla_2^2) - \frac{Z}{R_1} - \frac{Z}{R_2}$$

**Zeroth order Hamiltonian.
No electron – electron repulsion.**

$$\underline{H}' = \frac{1}{R_{12}}$$

**Perturbation piece of Hamiltonian.
Electron – electron repulsion.**

Need solutions to zeroth order equation

$$\underline{H}^0 \psi^0 = E^0 \psi^0$$

Take $\psi^0 = \psi^0(1)\psi^0(2)$

and $E^0 = E^0(1) + E^0(2)$

H⁰ has terms that depend only on 1 and 2. No cross terms. Can separate zeroth order equation into

$$\frac{1}{2} \nabla_1^2 \psi^0(1) + \left(E^0(1) + \frac{Z}{R_1} \right) \psi^0(1) = 0$$

$$\frac{1}{2} \nabla_2^2 \psi^0(2) + \left(E^0(2) + \frac{Z}{R_2} \right) \psi^0(2) = 0$$

These are equations for hydrogen like atoms with nuclear charge Z.

For ground state (1s)

$$\psi^0(1) = \frac{1}{\sqrt{\pi}} Z^{3/2} e^{-ZR_1}$$

$$\psi^0(2) = \frac{1}{\sqrt{\pi}} Z^{3/2} e^{-ZR_2}$$

Hydrogen 1s wavefunctions for electrons 1 and 2
but with nuclear charge Z .

The zeroth order solutions are

$$\psi^0(1,2) = \psi^0(1)\psi^0(2) = \frac{Z^3}{\pi} e^{-ZR_1} e^{-ZR_2}$$

product of 1s functions

$$E^0 = E^0(1) + E^0(2) = 2Z^2 E_{1s}(H)$$

sum of 1s energies with
nuclear charge Z

Correction to energy due to electron – electron repulsion

$$E' = H'_{nn} = H'_{1s,1s} \quad \text{expectation value of perturbation piece of } \underline{H}$$

$$= \iint \psi^{0*} \underline{H}' \psi^0 d\tau_1 d\tau_2$$

$$= \frac{e^2}{4\pi\epsilon_0 a_0} \frac{Z^6}{\pi^2} \iint \frac{e^{-2ZR_1} e^{-2ZR_2}}{R_{12}} d\tau_1 d\tau_2$$

Electron – electron repulsion depends on the distance between the two electrons.

$$d\tau_1 = \sin\theta_1 R_1^2 d\phi_1 d\theta_1 dR_1$$

spherical polar coordinates

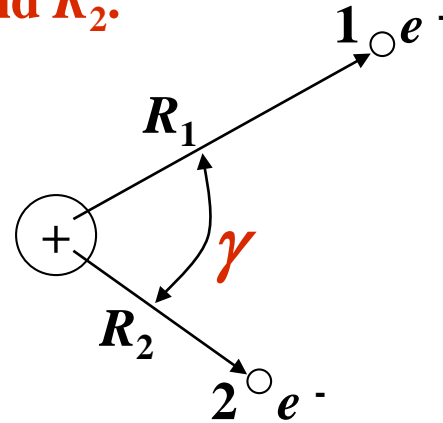
$$d\tau_2 = \sin\theta_2 R_2^2 d\phi_2 d\theta_2 dR_2$$

This is a tricky integral.

The following procedure can be used in this and analogous situations.

$$R_{12} = \sqrt{R_1^2 + R_2^2 - 2R_1R_2 \cos \gamma}$$

γ is the angle between the two vectors R_1 and R_2 .



Let $R_>$ be the greater of R_1 and R_2
 $R_<$ be the lesser of R_1 and R_2

Then $R_{12} = R_> \sqrt{1 + x^2 - 2x \cos \gamma}$

$$x = \frac{R_<}{R_>}$$

$$\frac{1}{R_{12}} = \frac{1}{R_{>}} \frac{1}{\sqrt{1+x^2-2x\cos(\gamma)}}$$

$$x = \frac{R_{<}}{R_{>}}$$

Expand in terms of Legendre polynomials (complete set of functions in $\cos(\gamma)$).

$$\frac{1}{R_{12}} = \frac{1}{R_{>}} \sum_n a_n P_n(\cos(\gamma))$$

The a_n can be found.

$$a_n = x^n$$

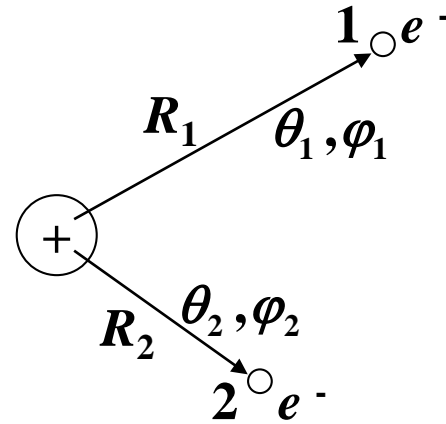
Therefore

$$\frac{1}{R_{12}} = \frac{1}{R_{>}} \sum_n x^n P_n(\cos(\gamma))$$

Now express the

$P_n(\cos(\gamma))$ in terms of the
 θ_1 & φ_1 ; θ_2 & φ_2

the absolute angles of the vectors
 rather than the relative angle.



The position of the two electrons can be written in terms of the
Spherical Harmonics, the solutions to the $\Phi(\varphi)$ and $\Theta(\theta)$ equations in the H atom.

$$P_n^{|m|}(\cos \theta_1) e^{im\varphi_1}$$

Complete set of angular functions.

$$P_n^{|m|}(\cos \theta_2) e^{im\varphi_2}$$

The result is

$$\frac{1}{R_{12}} = \sum_{\ell} \sum_m \frac{(\ell - |m|)!}{(\ell + |m|)!} \frac{R_{<}^{\ell}}{R_{>}^{\ell+1}} P_{\ell}^{|m|}(\cos \theta_1) P_{\ell}^{|m|}(\cos \theta_2) e^{im(\varphi_1 - \varphi_2)}$$

$$\frac{1}{R_{12}} = \sum_{\ell} \sum_m \frac{(\ell - |m|)!}{(\ell + |m|)!} \frac{R_{<}^{\ell}}{R_{>}^{\ell+1}} P_{\ell}^{|m|}(\cos \theta_1) P_{\ell}^{|m|}(\cos \theta_2) e^{im(\varphi_1 - \varphi_2)}$$

Here is the trick.

The ground state hydrogen wavefunctions (or any s orbitals) involve

$P_0^0(\cos \theta_1) e^{im\varphi_1}$ **1s wavefunctions have spherical harmonics with**

$P_0^0(\cos \theta_2) e^{im\varphi_2}$ $\ell = 0$ $m = 0$

These are constants. Each is just the normalization constant.

A constant times any spherical harmonic except the one with, $\ell = 0$ $m = 0$ which is a constant, integrated over the angles, gives zero.

Therefore, only the $\ell = 0$ $m = 0$ term in the sum survives when doing integral of each term in the sum.

The entire sum reduces to $\frac{1}{R_{>}}$ for 1s state or any s states.

For other states, limited number of terms. Group theory. Full rotation group. Integral of product of three functions. Direct product of representations of function must contain totally symmetric rep. Formulas exist.

Then

$$E' = \frac{e^2}{4\pi\epsilon_0 a_0} \frac{Z^6}{\pi^2} \iint \frac{e^{-2ZR_1} e^{-2ZR_2}}{R_{>}} d\tau_1 d\tau_2$$

The integral over angles yields $16\pi^2$.

$$E' = 16Z^6 \frac{e^2}{4\pi\epsilon_0 a_0} \int_0^\infty \int_0^\infty \frac{e^{-2ZR_1} e^{-2ZR_2}}{R_{>}} R_1^2 dR_1 R_2^2 dR_2$$

This can be written as

$$E' = \frac{16Z^6 e^2}{4\pi\epsilon_0 a_0} \int_0^\infty e^{-2ZR_1} \left[\frac{1}{R_1} \int_0^{R_1} e^{-2ZR_2} R_2^2 dR_2 + \int_{R_1}^\infty e^{-2ZR_2} R_2 dR_2 \right] R_1^2 dR_1$$

$R_1 > R_2$

$R_2 > R_1$

Doing the integrals yields

$$E' = \frac{5}{8} Z \frac{e^2}{4\pi\epsilon_0 a_0}$$

Putting back into normal units

$$E' = \left(-\frac{5}{4} Z \right) E_{1s}(H)$$

$$E_{1s}(H) = -\frac{1}{2} \frac{e^2}{4\pi\epsilon_0 a_0} = -13.6 \text{ eV}$$

Therefore,

$$E = E^0 + E' = \left(2Z^2 - \frac{5}{4} Z \right) E_{1s}(H)$$

negative number

Electron repulsion raises the energy.

For Helium, $Z = 2$, $E = -74.8 \text{ eV}$

<u>atom</u>	<u>exp. value (eV)</u>	<u>calc. value (eV)</u>	<u>% Error</u>
He	79.00	74.80	5.3
Li ⁺	198.09	193.80	2.2
Be ⁺²	371.60	367.20	1.2
B ⁺³	599.58	595.00	0.76
C ⁺⁴	882.05	877.20	0.55

Experimental values are the sum of the first and second ionization energies.
Ionization energy positive. Binding energy negative.

The Variational Method

The Variational Theorem:

If ϕ is any function such that

$$\int \phi^* \phi d\tau = 1 \quad (\text{normalized})$$

and if the lowest eigenvalue of the operator \underline{H} is E_0 ,
then

$$\langle \phi | \underline{H} | \phi \rangle = \int \phi^* \underline{H} \phi d\tau \geq E_0$$

The expectation value of \underline{H} or any operator for any function is always greater than or equal to the lowest eigenvalue.

Proof

Consider

$$\begin{aligned}\langle \phi | \underline{H} - E_0 | \phi \rangle &= \langle \phi | \underline{H} | \phi \rangle - \langle \phi | E_0 | \phi \rangle \\ &= \langle \phi | \underline{H} | \phi \rangle - E_0\end{aligned}$$

The true eigenkets of \underline{H} are

$$|\psi_i\rangle$$

$$\underline{H}|\psi_i\rangle = E_i|\psi_i\rangle$$

Expand $|\phi\rangle$ in terms of the $|\psi_i\rangle$

orthonormal basis set



$$|\phi\rangle = \sum_i c_i |\psi_i\rangle \quad \text{Expansion in terms of the eigenkets of } \underline{H}.$$

Substitute the expansion

$$\langle\phi|\underline{H} - E_0|\phi\rangle = \sum_i \bar{c}_i \langle\psi_i|(\underline{H} - E_0)\sum_j c_j |\psi_j\rangle$$

The $|\psi_j\rangle$ are eigenkets of $(\underline{H} - E_0)$. Therefore, the double sum collapses into a single sum.

$$= \sum_j \bar{c}_j c_j \langle\psi_j|(\underline{H} - E_0)|\psi_j\rangle$$

Operating \underline{H} on $|\psi_j\rangle$ returns E_j .

$$\langle\phi|\underline{H} - E_0|\phi\rangle = \sum_j \bar{c}_j c_j (E_j - E_0)$$

$$\langle \phi | \underline{H} - E_0 | \phi \rangle = \sum_j \bar{c}_j c_j (E_j - E_0)$$

$\bar{c}_j c_j \geq 0$ **A number times its complex conjugate is positive or zero.**

$E_j \geq E_0$ **An eigenvalue is greater than or equal to the lowest eigenvalue.**

Then,

$$(E_j - E_0) \geq 0$$

and $\sum_i \bar{c}_i c_i (E_i - E_0) \geq 0$

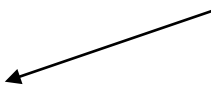
Therefore,

$$\langle \phi | \underline{H} - E_0 | \phi \rangle \geq 0$$

$$\langle \phi | \underline{H} - E_0 | \phi \rangle = \langle \phi | \underline{H} | \phi \rangle - E_0$$

Finally $\langle \phi | \underline{H} | \phi \rangle = \int \phi^* \underline{H} \phi d\tau \geq E_0$

The lower the energy you calculate, the closer it is to the true energy.



The equality holds only if $|\phi\rangle = |\psi_0\rangle$, the function is the lowest eigenfunction.

Using the Variational Theorem

Pick a trial function

$$\phi(\lambda_1, \lambda_2, \dots) \quad \text{normalized}$$

Calculate

$$J = \int \phi^* \underline{H} \phi d\tau$$

J is a function of the λ 's.

Minimize J (energy) with respect to the λ 's.

The minimized J - Approximation to E_0 .

The ϕ obtained from minimizing with respect to the λ 's - approximation to $|\psi_0\rangle$

Method can be applied to states above ground state with minor modifications.

Pick second function normalized and orthogonal to first function.

Minimize. If above first calculated energy, approximation to next highest energy.

If lower, it is the approximation to lowest state and initial energy is approx.

to the higher state energy.

Example - He Atom

Trial function

$$\phi = \frac{Z'^3}{\pi} e^{-Z'(R_1+R_2)}$$

The zeroth order perturbation function but with $Z \Rightarrow Z'$ a variable.

Writing \underline{H} as in perturbation treatment after substitutions

$$\underline{H} = -\frac{1}{2}(\nabla_1^2 + \nabla_2^2) - \frac{Z}{R_1} - \frac{Z}{R_2} + \frac{1}{R_{12}}$$

Rewrite by adding and subtracting $\frac{Z'}{R_1} + \frac{Z'}{R_2}$

$$\underline{H} = \left[-\frac{1}{2}(\nabla_1^2 + \nabla_2^2) - \frac{Z'}{R_1} - \frac{Z'}{R_2} \right] - (Z - Z') \left(\frac{1}{R_1} + \frac{1}{R_2} \right) + \frac{1}{R_{12}}$$

$$\underline{H} = \left[-\frac{1}{2}(\nabla_1^2 + \nabla_2^2) - \frac{Z'}{R_1} - \frac{Z'}{R_2} \right] - (Z - Z') \left(\frac{1}{R_1} + \frac{1}{R_2} \right) + \frac{1}{R_{12}}$$

Want to calculate

$$J = \int \phi^* \underline{H} \phi d\tau$$

using H from above.


The terms in red give

$$2Z'^2 E_{1s}(H)$$

Zeroth order perturbation energy with

$$Z \Rightarrow Z'$$

Therefore,

$$J = 2Z'^2 E_{1s}(H) - (Z - Z') \left[\iint \frac{\phi^2}{R_1} d\tau_1 d\tau_2 + \iint \frac{\phi^2}{R_2} d\tau_1 d\tau_2 \right] + \iint \frac{\phi^2}{R_{12}} d\tau_1 d\tau_2$$


These two integrals have the same value; only difference is subscript.

For the two integrals in brackets, performing integration over angles gives

$$2 \left[16\pi^2 \frac{Z'^6}{\pi^2} \int_0^\infty e^{-2Z'R_1} R_1 dR_1 \int_0^\infty e^{-2Z'R_2} R_2^2 dR_2 \right] = 2Z'$$

after doing the integrals over distance.

In conventional units $2Z' \frac{e^2}{4\pi\epsilon_0 a_0}$

The last term in the expression for J ($1/R_{12}$ term) was evaluated in the perturbation problem except $Z \Rightarrow Z'$.

The result is (in conventional units)

$$\frac{5}{8} Z' \frac{e^2}{4\pi\epsilon_0 a_0}$$

Putting the pieces together yields

$$J = 2Z'^2 E_{1s}(H) - (Z - Z')2Z' \frac{e^2}{4\pi\epsilon_0 a_0} + \frac{5}{8} Z' \frac{e^2}{4\pi\epsilon_0 a_0}$$

$$= \left[2Z'^2 + 4Z'(Z - Z') - \frac{5}{4} Z' \right] E_{1s}(H)$$

$$E_{1s}(H) = -\frac{1}{2} \frac{e^2}{4\pi\epsilon_0 a_0}$$

$$= \left[-2Z'^2 + 4ZZ' - \frac{5}{4} Z' \right] E_{1s}(H)$$

To get the best value of E for the trial function ϕ , minimize J with respect to Z' .

$$\frac{\partial J}{\partial Z'} = \left(-4Z' + 4Z - \frac{5}{4} \right) E_{1s}(H) = 0$$

Solving for Z' yields

$$Z' = Z - \frac{5}{16} \quad \text{and} \quad Z = Z' + \frac{5}{16}$$

Using this value to eliminate Z in the expression for J

$$J = \left[-2Z'^2 + 4ZZ' - \frac{5}{4}Z' \right] E_{1s}(H)$$

yields

$$E = 2Z'^2 E_{1s}(H)$$

This is the approximate energy of the ground state of the He atom ($Z = 2$) or two electron ions ($Z > 2$).

<u>atom</u>	<u>exp. value (eV)</u>	<u>calc. value (eV)</u>	<u>% Error</u>
He	79.00	77.46	1.9
Li ⁺	198.09	196.46	0.82
Be ⁺²	371.60	369.86	0.47
B ⁺³	599.58	597.66	0.32
C ⁺⁴	882.05	879.86	0.15

He perturbation theory value – 74.8 eV